A Modern Course in Statistical Physics

2nd Edition

L. E. REICHL

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This book is dedicated to
Ilya Prigogine
for his encouragement and support
and because
he has changed our view of the world.

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PREFACE

In 1992 after finishing my book, "The Transition of Chaos," I realized that I needed to write a new edition of "A Modern Course in Statistical Physics". I wanted to adjust the material to better prepare students for what I believe are the current directions of statistical physics. I wanted to place more emphasis on nonequilibrium processes and on the thermodynamics underlying biological processes. I also wanted to be more complete in the presentation of material. It turned out to be a greater task than I had anticipated, and now five years later I am finally finishing the second edition. One reason it has taken so long is that I have created a detailed solution manual for the second edition and I have added many worked out exercises to the text. In this way I hope I have made the second edition much more student and instructor friendly than the first edition was.

There are two individuals who have had a particularly large influence on this book and whom I want to thank, even though they took no part in writing the book. (Any negative features of this book are totally my responsibility.) The biggest influence has been Ilya Prigogine, and for that reason I have dedicated this book to him. When I first came to the University of Texas to join the Physics faculty, I became a member of what was then the Center for Thermodynamics and Statistical Mechanics (now known as the Prigogine Center for Statistical Mechanics and Complex Systems). My training was in equilibrium statistical mechanics. But that changed when I learned that the focus of this unique research Center, deep in the heart of Texas, was on nonequilibrium nonlinear phenomena, most of it far from equilibrium. I began to work on nonequilibrium and nonlinear phenomena, but followed my own path. The opportunity to teach and work in this marvelous research center and to listen to the inspiring lectures of Ilya Prigogine and lectures of the many visitors to the Center has opened new worlds to me, some of which I have tried to bring to students through this book.

The other individual who has had a large influence on this book is Nico van Kampen, a sometimes visitor to the University of Texas. His beautiful lectures on stochastic processes were an inspiration and spurred my interest in the subject.

I want to thank the many students in my statistical mechanics classes who helped me shape the material for this book and who also helped me correct the manuscript.

This book covers a huge range of material. I could not reference all the work by the individuals who have contributed in all these areas. I have referenced work which most influenced my view of the subject and which could lead students to other related work. I apologize to those whose work I have not been able to include in this book.

L. E. Reichl

Austin, Texas
September 1997

1

INTRODUCTION

1.A. OVERVIEW

The field of statistical physics has expanded dramatically in recent years. New results in ergodic theory, nonlinear chemical physics, stochastic theory, quantum fluids, critical phenomena, hydrodynamics, transport theory, and biophysics have revolutionized the subject, and yet these results are rarely presented in a form that students who have little background in statistical physics can appreciate or understand. This book has been written in an effort to incorporate these subjects into a basic course on statistical physics. It includes in a unified and integrated manner the foundations of statistical physics and develops from them most of the tools needed to understand the concepts underlying modern research in all of the above fields.

In the field of ergodic theory, for example, chaos theory has deepened our understanding of the structure and dynamical behavior of a variety of nonlinear systems and has made ergodic theory a modern field of research. Indeed, one of the frontiers of science today is the study of the spectral properties of decay processes in nature, based on the chaotic nature of the underlying dynamics of those systems. Advances in this field have been aided by the development of ever more powerful computers. In an effort to introduce this field to students, a careful discussion is given of the behavior of probability flows in phase space, including specific examples of ergodic and mixing flows.

Nonlinear chemical physics is still in its infancy, but it has already given a conceptual framework within which we can understand the thermodynamic origin of life processes. The discovery of *dissipative structures* (nonlinear spatial and temporal structures) in nonlinear nonequilibrium chemical systems has opened a new field in chemistry and biophysics. In this book, material has been included on chemical thermodynamics, chemical hydrodynamics, and nonequilibrium phase transitions in chemical and hydrodynamic systems.

The use of stochastic theory to study fluctuation phenomena in chemical and hydrodynamic systems, along with its growing use in population dynamics and complex systems theory, has brought new life to this field. The discovery of scaling behavior at all levels of the physical world, along with the appearance of Levy flights which often accompanies scaling behavior, has forced us to think

beyond the limits of the Central Limit Theorem. In order to give students some familiarity with modern concepts from the field of stochastic theory, we have placed probability theory in a more general framework and discuss, within that framework, classical random walks, Levy flights, and Brownian motion.

The theory of superfluids rarely appears in general textbooks on statistical physics, but the theory of such systems is incorporated at appropriate places throughout this book. We discuss the thermodynamic properties of superfluid and superconducting systems, the Ginzburg–Landau theory of superconductors, the BCS theory of superconductors, and superfluid hydrodynamics. Also included in the book is an extensive discussion of properties of classical fluids and their thermodynamic and hydrodynamic properties.

The theory of phase transitions has undergone a revolution in recent years. In this book we define critical exponents and use renormalization theory to compute them. We also derive an exact expression for the specific heat of the two-dimensional Ising system, one of the simplest exactly solvable systems which can exhibit a phase transition. At the end of the book we include an introduction to the theory of nonequilibrium phase transitions.

Hydrodynamics is a very powerful tool for understanding long-wavelength phenomena in classical fluids, solids, liquid crystals, superfluids, and biological systems. This book contains a thorough grounding in hydrodynamics based on the underlying symmetries and stability properties of matter. We discuss properties of correlation functions, causality, the fluctuation–dissipation theorem, the theory of light scattering, and the origin of hydrodynamics in terms of conserved quantities and broken symmetries. We also include a variety of applications of the hydrodynamics of mixtures, a subject essential for biophysics.

Transport theory is discussed from many points of view. We derive Onsager's relations for transport coefficients. We derive expressions for transport coefficients based on simple "back of the envelope" mean free path arguments. The Boltzmann and Lorentz–Boltzmann equations are derived and microscopic expressions for transport coefficients are obtained, starting from spectral properties of the Boltzmann and Lorentz–Boltzmann collision operators. The difficulties in developing a convergent transport theory for dense gases are also reviewed.

Concepts developed in statistical physics underlie all of physics. Once the forces between microscopic particles are determined, statistical physics gives us a picture of how microscopic particles act in the aggregate to form the macroscopic world. As we see in this book, what happens on the macroscopic scale is sometimes surprising.

1.B. PLAN OF BOOK

Thermodynamics is a consequence and a reflection of the symmetries of nature. It is what remains after collisions between the many degrees of freedom of

macroscopic systems randomize and destroy most of the coherent behavior. The quantities which cannot be destroyed, due to underlying symmetries of nature and their resulting conservation laws, give rise to the *state variables* upon which the theory of thermodynamics is built. Thermodynamics is therefore a solid and sure foundation upon which we can construct theories of matter out of equilibrium. That is why we place heavy emphasis on it in this book.

The book is divided into four parts. Chapters 2 and 3 present the foundations of thermodynamics and the thermodynamics of phase transitions. Chapters 4 through 6 present probability theory, stochastic theory, and the foundations of statistical mechanics. Chapters 7 through 9 present equilibrium statistical mechanics, with emphasis on phase transitions and the equilibrium theory of classical fluids. Chapters 10 through 12 deal with nonequilibrium processes, both on the microscopic and macroscopic scales, both near and far from equilibrium. The first two parts of the book essentially lay the foundations for the last two parts.

There seems to be a tendency in many books to focus on equilibrium statistical mechanics and derive thermodynamics as a consequence. As a result, students do not get the experience of traversing the vast world of thermodynamics and do not understand how to apply it to systems which are too complicated for statistical mechanics. For this reason, we begin the book with a thorough grounding in thermodynamics. In Chapter 2 we review the foundations of thermodynamics and thermodynamic stability theory and devote a large part of the chapter to a variety of applications which do not involve phase transitions, such as the cooling of gases, mixing, osmosis, and chemical thermodynamics. Chapter 3 is devoted to the thermodynamics of phase transitions and the use of thermodynamic stability theory in analyzing these phase transitions. We discuss first-order phase transitions in liquid–vapor–solid transitions, with particular emphasis on the liquid–vapor transition and its critical point and critical exponents. We also introduce the Ginzburg–Landau theory of continuous phase transitions and discuss a variety of transitions which involve broken symmetries.

Having developed some intuition concerning the macroscopic behavior of complex equilibrium systems, we then turn to microscopic foundations. Chapters 4 through 6 are devoted to probability theory and the foundations of statistical mechanics. Chapter 4 contains a review of basic concepts from probability theory and then uses these concepts to describe classical random walks and Levy flights. The Central Limit Theorem and the breakdown of the Central Limit Theorem for scaling processes is described. In Chapter 5 we study the dynamics of discrete stochastic variables based on the master equation. We also introduce the theory of Brownian motion and the idea of separation of time scales, which has proven so important in describing nonequilibrium phase transitions. The theory developed in Chapter 5 has many applications in chemical physics, laser physics, population dynamics, and biophysics, and it prepares the way for more complicated topics in statistical mechanics.

Chapter 6 lays the probabilistic foundations of statistical mechanics, starting from ergodic theory. In recent years, there has been a tendency to sidestep this aspect of statistical physics completely and to introduce statistical mechanics using information theory. The student then misses one of the current frontiers of modern physics, the study of the spectral behavior of decay processes in nature, based on the chaotic nature of the underlying dynamics of those systems. While we cannot go very far into this subject in this book, we at least discuss the issues. We begin by deriving the Liouville equation, which is the equation of motion for probability densities, both in classical mechanics and in quantum mechanics. We look at the types of flow that can occur in mechanical systems and introduce the concepts of ergodic and mixing flows, which appear to be minimum requirements if a system is to decay to thermodynamic equilibrium.

Chapters 7–9 are devoted entirely to equilibrium statistical mechanics. In Chapter 7 we derive the probability densities (the microcanonical, canonical, and grand canonical ensembles) for both closed and opened systems and relate them to thermodynamic quantities and the theory of fluctuations. We then use them to derive the thermodynamic properties of a variety of model systems, including harmonic lattices, spin systems, ideal quantum gases, and superconductors.

In Chapter 8 we introduce the equilibrium fluctuation theory of spin systems and show qualitatively how the spatial extent of correlations between fluctuations diverges as we approach the critical point. We also introduce the idea of scaling and use renormalization theory to obtain microscopic expressions for the critical exponents of spin lattices. Finally we conclude Chapter 8 by obtaining an exact expression for the heat capacity of the two-dimensional Ising lattice, and we compare our exact expressions to those of mean field theory.

Chapter 9 is devoted to the equilibrium theory of classical fluids. In this chapter we relate the thermodynamic properties of classical fluids to the underlying radial distribution function, and we use the Ursell–Mayer cluster expansion to obtain a virial expansion of the the equation of state of a classical fluid. We also discuss how to include quantum corrections for nondegenerate gases.

The last part of the book, Chapters 10–12, deals with nonequilibrium processes. Chapter 10 is devoted to hydrodynamic processes for systems near equilibrium. We begin by deriving the Navier–Stokes equations from the symmetry properties of a fluid of point particles, and we use the derived expression for entropy production to obtain the transport coefficients for the system. We use the solutions of the linearized Navier–Stokes equations to predict the outcome of light-scattering experiments. We go on to derive Onsager's relations between transport coefficients, and we use causality to derive the fluctuation–dissipation theorem. We also derive a general expression for the entropy production in systems with mixtures of particles which can undergo chemical reactions. We then use this theory to describe thermal and chemical transport processes in mixtures, across membranes, and in electrical circuits. The hydrodynamic equations describe the behavior of just a few slowly

varying degrees of freedom in fluid systems. If we assume that the remainder of the fluid can be treated as a background noise, we can use the fluctuation–dissipation theorem to derive the correlation functions for this background noise. In Chapter 10 we also consider hydrodynamic modes which result from broken symmetries, and we derive hydrodynamic equations for superfluids and consider the types of sound that can exist in such fluids.

In Chapter 11 we derive microscopic expressions for the coefficients of diffusion, shear viscosity, and thermal conductivity, starting both from mean free path arguments and from the Boltzmann and Lorentz–Boltzmann equations. In deriving microscopic expressions for the transport coefficients from the Boltzmann and Lorentz–Boltzmann equations, we use a very elegant method which relies on use of the eigenvalues and eigenfunctions of the collision operators associated with those equations. We obtain explicit microscopic expressions for the transport coefficients of a hard sphere gas.

Finally, in Chapter 12 we conclude with the fascinating subject of nonequilibrium phase transitions. We discuss thermodynamic stability theory for systems far from equilibrium. We also show how nonlinearities in the rate equations for chemical reaction–diffusion systems lead to nonequilibrium phase transitions which give rise to chemical clocks, nonlinear chemical waves, and spatially periodic chemical structures, while nonlinearities in the Rayleigh–Benard hydrodynamic system lead to spatially periodic convection cells. We shall also examine the nature of fluctuations in the neighborhood of the critical point for these transitions and show that they are characterized by a critical slowing down of certain unstable modes.

1.C. USE AS A TEXTBOOK

Even though this book contains a huge amount of material, it has been designed to be used as a textbook. In each chapter the material has been divided into *core topics* and *special topics*. The core topics provide key basic material in each chapter, while special topics illustrate these core ideas with a variety of applications. The instructor can select topics from the special topics sections, according to the emphasis he/she wishes to give the course.

In many sections, we have included nontrivial demonstration exercises to help the students understand the material and to help in solving homework problems. Each chapter has a variety of problems at the end of the chapter that can be used to help the students test their understanding.

Even if one covers only the core topics of each chapter, there may be too much material to cover in a one-semester course. However, the book is designed so that some chapters may be omitted completely. The choice of which chapters to use depends on the interests of the instructor. Our suggestion for a basic well-rounded one-semester course in statistical physics is to cover the core topics in Chapters 2, 3, 4, 7, 10, and 11 (only Section 11.B if time is running short).

The book is intended to introduce the students to a variety of subjects and resource materials which they can then pursue in greater depth if they wish. We have tried to use standardized notation as much as possible. In writing a book which surveys the entire field of statistical physics, it is impossible to include or even to reference everyone's work. We have included references which were especially pertinent to the points of view we take in this book and which will lead students easily to other work in the same field.

PART ONE

THERMODYNAMICS

2

INTRODUCTION TO THERMODYNAMICS

2.A. INTRODUCTORY REMARKS

The science of thermodynamics began with the observation that matter in the aggregate can exist in macroscopic states which are stable and do not change in time. These stable "equilibrium" states are characterized by definite mechanical properties, such as color, size, and texture, which change as the substance becomes hotter or colder (changes its temperature). However, any given equilibrium state can always be reproduced by bringing the substance back to the same state. Once a system reaches its equilibrium state, all changes cease and the system will remain forever in that state unless some external influence acts to change it. This inherent stability and reproducibility of the equilibrium states can be seen everywhere in the world around us.

Thermodynamics has been able to describe, with remarkable accuracy, the macroscopic behavior of a huge variety of systems over the entire range of experimentally accessible temperatures (10^{-4} K to 10^{6} K). It provides a truly universal theory of matter in the aggregate. And yet, the entire subject is based on only four laws, which may be stated rather simply as follows: Zeroth Law—it is possible to build a thermometer; First Law—energy is conserved; Second Law—not all heat energy can be converted into work; and Third Law—we can never reach the coldest temperature using a finite set of reversible steps. However, even though these laws sound rather simple, their implications are vast and give us important tools for studying the behavior and stability of systems in equilibrium and, in some cases, of systems far from equilibrium.

The *core topics* in this chapter focus on a review of various aspects of thermodynamics that will be used throughout the remainder of the book. The *special topics* at the end of this chapter give a more detailed discussion of some applications of thermodynamics which do not involve phase transitions. Phase transitions will be studied in Chapter 3.

We shall begin this chapter by introducing the variables which are used in thermodynamics and the mathematics needed to calculate changes in the thermodynamic state of a system. As we shall see, many different sets of

mechanical variables can be used to describe thermodynamic systems. In order to become familiar with some of these mechanical variables, we shall write the experimentally observed equations of state for a variety of thermodynamic systems.

As we have mentioned above, thermodynamics is based on four laws. We shall discuss the content of these laws in some detail, with particular emphasis on the second law. The second law is extremely important both in equilibrium and out of equilibrium because it gives us a criterion for testing the stability of equilibrium systems and, in some cases, nonequilibrium systems.

There are a number of different thermodynamic potentials that can be used to describe the behavior and stability of thermodynamic systems, depending on the type of constraints imposed on the system. For a system which is isolated from the world, the internal energy will be a minimum for the equilibrium state. However, if we couple the system thermally, mechanically, or chemically to the outside world, other thermodynamic potentials will be minimized. We will introduce the five most commonly used thermodynamic potentials (internal energy, enthalpy, Helmholtz free energy, Gibbs free energy, and the grand potential), and we will discuss the conditions under which each one is minimized at equilibrium and why they are called potentials.

When experiments are performed on thermodynamic systems, the quantities which are easiest to measure are the response functions. Generally, we change one parameter in the system and see how another parameter responds to that change, under highly controlled conditions. The quantity that measures the way in which the system responds is called a *response function.* In this chapter we shall introduce a variety of thermal and mechanical response functions and give relations between them.

Isolated equilibrium systems are systems in a state of maximum entropy. Any fluctuations which occur in such systems must cause a decrease in entropy if the equilibrium state is to be stable. We can use this fact to find relations between the intensive state variables for different parts of a system if those parts are to be in mechanical, thermal, and chemical equilibrium. In addition, we can find restrictions on the sign of the response functions which must be satisfied for stable equilibrium. We shall find these conditions and discuss the restrictions they place on the Helmholtz and Gibbs free energy.

Thermodynamics becomes most interesting when it is applied to real systems. In order to demonstrate its versatility, in the section on special topics, we shall apply it to a number of systems which have been selected for their practical importance or conceptual importance.

We begin with a subject of great practical and historic importance, namely, the cooling of gases. it is often necessary to cool substances below the temperature of their surroundings. The refrigerator most commonly used for this purpose is based on the Joule–Kelvin effect. There are two important ways to cool gases. We can let them do work against their own intermolecular forces by letting them expand freely (Joule effect); or we can force them through a small constriction, thus causing cooling at low temperatures or heating at high

temperatures (Joule-Kelvin effect). The Joule-Kelvin effect is by far the more effective of the two methods. We shall discuss both methods in this chapter and use the van der Waals equation of state to obtain estimates of the coolling effects for some real gases.

For reversible processes, changes in entropy content can be completely accounted for in terms of changes in heat content. For irreversible processes, this is no longer true. We can have entropy increase in an isolated system, even though no heat has been added. Therefore, it is often useful to think of an increase in entropy as being related to an increase in disorder in a system. One of the most convincing illustrations of this is the entropy change which occurs when two substances, which have the same temperature and pressure but different identities, are mixed. Thermodynamics predicts that the entropy will increase solely due to mixing of the substances.

When the entropy of a system changes due to mixing, so will other thermodynamic quantities. One of the most interesting examples of this is osmosis. We can fill a container with water and separate it into two parts by a membrane permeable to water but not salt, for example. If we put a small amount of salt into one side, the pressure of the resulting salt solution will increase markedly because of mixing.

Chemical reactions can be characterized in a rather simple way in terms of a thermodynamic quantity called the *affinity*. The affinity gives a measure of the distance of a chemical reaction from thermodynamic equilibrium and will be useful in later chapters when we discuss chemical systems out of equilibrium. We can obtain an expression for the affinity by using the conditions for thermodynamic equilibrium and stability introduced in Chapter 2, and at the same time we can learn a number of interesting facts about the thermodynamic behavior of chemical reactions. A special example of a type of reaction important to biological systems is found in electrolytes, which consist of salts which can dissociate but maintain an electrically neutral solution.

2.B. STATE VARIABLES AND EXACT DIFFERENTIALS

Thermodynamics describes the behavior of systems with many degrees of freedom after they have reached a state of thermal equilibrium—a state in which all past history is forgotten and all macroscopic quantities cease to change in time. The amazing feature of such systems is that, even though they contain many degrees of freedom ($\sim 10^{23}$) in chaotic motion, their thermodynamic state can be specified completely in terms of a few parameters—called *state variables*. In general, there are many state variables which can be used to specify the thermodynamic state of a system, but only a few (usually two or three) are independent. In practice, one chooses state variables which are accessible to experiment and obtains relations between them. Then, the "machinery" of thermodynamics enables one to obtain the values of any other state variables of interest.

State variables may be either *extensive* or *intensive*. Extensive variables always change in value when the size (spatial extent and number of degrees of freedom) of the system is changed, and intensive variables need not. Certain pairs of intensive and extensive state variables often occur together because they correspond to generalized forces and displacements which appear in expressions for thermodynamic work. Some examples of such extensive and intensive pairs are, respectively, volume, V, and pressure, P; magnetization, $\mathbf{M}$, and magnetic field strength, $\mathbf{H}$; length, L, and tension, J; area, A, and surface tension, σ; electric polarization, $\mathbf{P}$, and electric field, $\mathbf{E}$. The pair of state variables related to heat content of thermodynamic system are the temperature, T, which is intensive, and the entropy, S, which is extensive. There is also a pair of state variables associated with "chemical" properties of a system. They are the number of particles, N, which is extensive, and the chemical potential per particle, μ', which is intensive. In this book we shall sometimes use the number of moles, n, and the chemical potential per mole, μ (molar chemical potential); or the mass of a substance, M, and the chemical potential per unit mass, $\tilde{\mu}$, (specific chemical potential), as the chemical state variables. If there is more than one type of particle in the system, then there will be a·mole number and chemical potential associated with each type of particle.

Other state variables used to describe the thermodynamic behavior of a system are the various response functions, such as heat capacity, C; compressibility, κ; magnetic susceptibility, χ; and various thermodynamic potentials, such as the internal energy, U; enthalpy, H; Helmholtz free energy, A; Gibbs free energy, G; and the grand potential, Ω. We shall become thoroughly acquainted with these state variables in subsequent sections.

If we change the thermodynamic state of our system, the amount by which the state variables change must be independent of the path taken. If this were not so, the state variables would contain information about the history of the system. It is precisely this property of state variables which makes them so useful in studying changes in the equilibrium state of various systems. Mathematically changes in state variables correspond to exact differentials [1]; therefore, before we begin our discussion of thermodynamics, it is useful to review the theory of exact differentials. This will be the subject of the remainder of this section.

Given a function $F = F(x_1, x_2)$ depending on two independent variables x_1 and x_2, the differential of F is defined as follows:

$$dF = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} dx_1 + \left(\frac{\partial F}{\partial x_2}\right)_{x_1} dx_2, \tag{2.1}$$

where $(\partial F/\partial x_1)_{x_2}$ is the derivative of F with respect to x_1 holding x_2 fixed. If F and its derivatives are continuous and

$$\left[\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right]_{x_2} = \left[\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right]_{x_1}, \tag{2.2}$$

then dF is an exact differential. If we denote

$$c_1(x_1,x_2) \equiv \left(\frac{\partial F}{\partial x_1}\right)_{x_2} \quad \text{and} \quad c_2(x_1,x_2) \equiv \left(\frac{\partial F}{\partial x_2}\right)_{x_1},$$

then the variables c_1 and x_1 and variables c_2 and x_2 are called "conjugate" variables with respect to the function F.

The fact that dF is exact has the following consequences:

(a) The value of the integral

$$F(B) - F(A) = \int_A^B dF = \int_A^B (c_1 dx_1 + c_2\, dx_2)$$

is independent of the path taken between A and B and depends only on the end points A and B.

(b) The integral of dF around a closed path is zero:

$$\oint_{\text{closed}} dF = \oint_{\text{closed}} (c_1 dx_1 + c_2 dx_2) \equiv 0.$$

(c) If one knows only the differential dF, then the function F can be found to within an additive constant.

If F depends on more than two variables, then the statements given above generalize in a simple way: Let $F = F(x_1, x_2, \ldots, x_n)$, then the differential, dF, may be written

$$dF = \sum_{i=1}^{n} \left(\frac{\partial F}{\partial x_i}\right)_{\{x_{j\neq i}\}} dx_i. \tag{2.3}$$

The notation $(\partial F/\partial x_i)_{\{x_{j\neq i}\}}$ means that the derivative of F is taken with respect to x_i holding *all* variables *but* x_i constant. For any pair of variables, the following relation holds:

$$\left[\frac{\partial}{\partial x_l}\left(\frac{\partial F}{\partial x_k}\right)_{\{x_{j\neq k}\}}\right]_{\{x_{j\neq l}\}} = \left[\frac{\partial}{\partial x_k}\left(\frac{\partial F}{\partial x_l}\right)_{\{x_{j\neq l}\}}\right]_{\{x_{j\neq k}\}}. \tag{2.4}$$

An example for the case of three independent variables is

$$dF = c_1 dx_1 + c_2 dx_2 + c_3 dx_3.$$

The Eq. (2.4) leads to the result

$$\left(\frac{\partial c_1}{\partial x_2}\right)_{x_1,x_3} = \left(\frac{\partial c_2}{\partial x_1}\right)_{x_2,x_3}, \left(\frac{\partial c_1}{\partial x_3}\right)_{x_1,x_2} = \left(\frac{\partial c_3}{\partial x_1}\right)_{x_3,x_2},$$

$$\left(\frac{\partial c_2}{\partial x_3}\right)_{x_2,x_1} = \left(\frac{\partial c_3}{\partial x_2}\right)_{x_3,x_1}.$$

Differentials of all state variables are exact and have the above properties. Given four state variables, x, y, z, and w, where w is a function of any two of the variables x, y, or z, one can obtain the following useful relations along paths for which $F(x, y, z) = 0$:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}. \tag{2.5}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{2.6}$$

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z. \tag{2.7}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z. \tag{2.8}$$

It is a simple matter to derive Eqs. (2.5)–(2.8). We will first consider Eqs. (2.5) and (2.6). Let us choose variables y and z to be independent, $x = x(y, z)$, and then choose x and z to be independent, $y = y(x, z)$, and write the following differentials; $dx = (\partial x/\partial y)_z dy + (\partial x/\partial z)_y dz$ and $dy = (\partial y/\partial x)_z dx + (\partial y/\partial z)_x dz$.

If we eliminate dy between these equations, we obtain

$$\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1\right] dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz = 0.$$

Because dx and dz may be varied independently, their coefficients may be set equal to zero separately. The result is Eqs. (2.5) and (2.6).

To derive Eq. (2.7) we let y and z be independent so that $x = x(y, z)$ and write the differential for dx. If we then divide by dw, we obtain

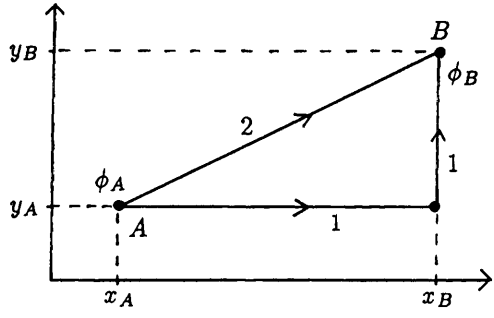
$$\frac{dx}{dw} = \left(\frac{\partial x}{\partial y}\right)_z \frac{dy}{dw} + \left(\frac{\partial x}{\partial z}\right)_y \frac{dz}{dw}.$$

For constant $z, dz = 0$ and we find Eq. (2.7)

Finally, to derive Eq. (2.8) we let x be a function of y and w, $x = x(y, w)$. If we write the differential of x, divide it by dy, and restrict the entire equation to constant z, we obtain Eq. (2.8).

When integrating exact differentials, one must be careful not to lose terms. In Exercise 2.1, we illustrate two different methods for integrating exact differentials.

■ **EXERCISE 2.1.** Consider the differential $d\phi = (x^2 + y)dx + xdy$. (a) Show that it is an exact differential. (b) Integrate $d\phi$ between the points A and B in the figure below, along the two different paths, 1 and 2. (c) Integrate $d\phi$ between points A and B using indefinite integrals.



Answer:

(a) From the expression $d\phi = (x^2 + y)dx + xdy$, we can write $(\partial\phi/\partial x)_y = x^2 + y$ and $(\partial\phi/\partial y)_x = x$. Since $[(\partial/\partial y)(\partial\phi/\partial x)_y]_x = [(\partial/\partial x)(\partial\phi/\partial y)_x]_y = 1$, the differential, $d\phi$, is exact.

(b) Let us first *integrate the differential, $d\phi$, along path 1:*

$$\begin{aligned}\phi_B - \phi_A &= \int_{x_A}^{x_B} (x^2 + y_A)\,dx + \int_{y_A}^{y_B} x_B\,dy \\ &= \tfrac{1}{3}x_B^3 + x_B y_B - \tfrac{1}{3}x_A^3 - x_A y_A.\end{aligned} \tag{1}$$

Let us next *integrate the differential, $d\phi$, along path* 2. Note that along *path* 2, $y = y_A + (\Delta y/\Delta x)(x - x_A)$, where $\Delta y = y_B - y_A$ and $\Delta x = x_B - x_A$. If we substitute this into the expression for $d\phi$, we find $d\phi = (x^2 + y)dx + xdy = [x^2 + y_A + (\Delta y/\Delta x)(2x - x_A)]dx$. Therefore

$$\begin{aligned}\phi_B - \phi_A &= \int_{x_A}^{x_B} dx\left[x^2 + y_A + \frac{\Delta y}{\Delta x}(2x - x_A)\right] \\ &= \tfrac{1}{3}x_B^3 + x_B y_B - \tfrac{1}{3}x_A^3 - x_A y_A.\end{aligned} \tag{2}$$

Note that the change in ϕ in going from point A to point B is independent of the path taken. This is a property of exact differentials.

(c) We now integrate the differential, $d\phi$, in a different way. Let us first do the indefinite integrals

$$\int \left(\frac{\partial \phi}{\partial x}\right)_y dx = \int (x^2 + y) dx = \tfrac{1}{3}x^3 + xy + K_1(y), \tag{3}$$

where $K_1(y)$ is an unknown function of y. Next do the integral

$$\int \left(\frac{\partial \phi}{\partial y}\right)_x dy = \int x dy = xy + K_2(x), \tag{4}$$

where $K_2(x)$ is an unknown function of x. In order for Eqs. (3) and (4) to be consistent, we must choose $K_2(x) = \frac{1}{3}x^3 + K_3$ and $K_1(y) = K_3$, where K_3 is a constant. Therefore, $\phi = \frac{1}{3}x^3 + xy + K_3$ and again, $\phi_B - \phi_A = \frac{1}{3}x_B^3 + x_B y_B - \frac{1}{3}x_A^3 - x_A y_A$.

2.C. SOME MECHANICAL EQUATIONS OF STATE

An equation of state is a functional relation between the state variables for a system in equilibrium which reduces the number of independent degrees of freedom needed to describe the state of the system. It is an equation which relates the thermal state variables, T or S, to the mechanical and chemical state variables for that system and contains a great deal of information about the thermodynamic behavior of the system. It is useful to give some examples of empirically obtained equations of state.

2.C.1. Ideal Gas Law

The best-known equation of state is the ideal gas law

$$PV = nRT, \tag{2.9}$$

where n is the number of moles, T is temperature in degrees Kelvin, P is the pressure in Pascals, V is the volume in cubic meters, and $R = 8.314$ J/mol· K is the universal gas constant. The ideal gas law gives a good description of a gas which is so dilute that the effect of interaction between particles can be neglected.

If there are m different types of particles in the gas, then the ideal gas law takes the form

$$PV = \sum_{i=1}^{m} n_i RT, \tag{2.10}$$

where n_i is the number of moles of the ith constituent.

2.C.2. Virial Expansion [2]

The virial expansion,

$$P = \left(\frac{nRT}{V}\right)\left[1 + \frac{n}{V}B_2(T) + \left(\frac{n}{V}\right)^2 B_3(T) + \cdots\right], \tag{2.11}$$

expresses the equation of state of a gas as a density expansion. The quantities $B_2(T)$ and $B_3(T)$ are called the second and third virial coefficients and are functions of temperature only. As we shall see in Chapter 9, the virial coefficients may be computed in terms of the interparticle potential. Comparison between experimental and theoretical values for the virial coefficients is an important method for obtaining the force constants for various interparticle potentials. In Fig. 2.1 we have plotted the second virial coefficient for helium and argon. The curves are typical of most gases. At low temperatures, B_2(T) is negative because the kinetic energy is small and the attractive forces between particles reduce the pressure. At high temperatures the attractive forces have little effect and corrections to the pressure become positive. At high temperature the second virial coefficient has a maximum.

For an ideal classical gas all virial coefficients, $B_i (i \geq 2)$, are zero, but for an ideal quantum gas (Bose–Einstein or Fermi–Dirac) the virial coefficients are

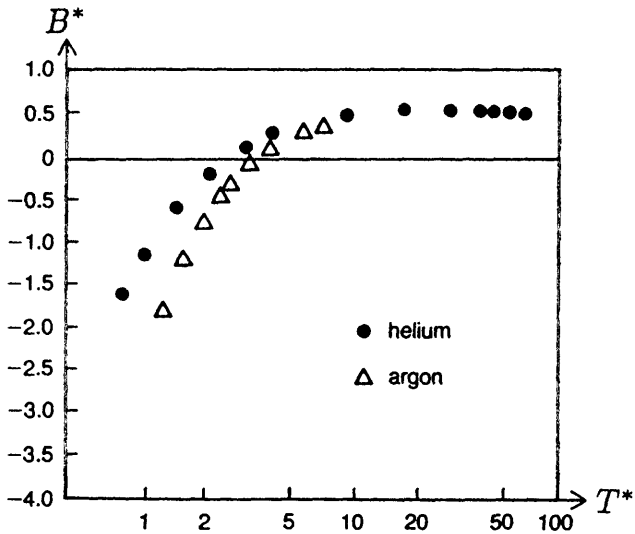


Fig. 2.1. A plot of the second virial coefficients for helium and argon in terms of the dimensionless quantities, $B^* = B_2/b_0$ and $T^* = k_B T/\varepsilon$, where b_0 and ε are constants, k_B is Boltzmann's constant, and T is the temperature. For helium, $b_0 = 21.07 \times 10^{-6}\text{m}^3/\text{mol}$ and $\varepsilon/k_B = 10.22$ K. For argon, $b_0 = 49.8 \times 10^{-6}\text{m}^3/\text{mol}$ and $\varepsilon/k_B = 119.8$ K. (Based on Ref. 2.)

nonzero. The "statistics" of quantum particles give rise to corrections to the classical ideal gas equation of state.

2.C.3. Van der Waals Equation of State [3]

The van der Waals equation of state is of immense importance historically because it was the first equation of state which applies to both the gas and liquid phases and exhibits a phase transition. It contains most of the important qualitative features of the gas and liquid phases although it becomes less accurate as density increases. The van der Waals equation contains corrections to the ideal gas equation of state, which take into account the form of the interaction between real particles. The interaction potential between molecules in a gas contains a strong repulsive core and a weaker attractive region surrounding the repulsive core. For an ideal gas, as the pressure is increased, the volume of the system can decrease without limit. For a real gas this cannot happen because the repulsive core limits the close-packed density to some finite value. Therefore, as pressure is increased, the volume tends to some minimum value, $V = V_{min} = nb$, where b is an experimental constant. The ideal gas equation of state must be corrected to take account of the existence of the repulsive core and assumes the form

$$P = \frac{nRT}{V - nb}.$$

The attracive region of the potential causes the pressure to be decreased slightly relative to that of a noninteracting gas because it introduces a "cohesion" between molecules. The decrease in pressure will be proportional to the probability that two molecules interact; this, in turn, is proportional to the square of the density of particles $(N/V)^2$. We therefore correct the pressure by a factor proportional to the square of the density, which we write $a(n^2/V^2)$. The constant a is an experimental constant which depends on the type of molecule being considered. The equation of state can now be written

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT. \tag{2.12}$$

In Table 2.1 we have given values of a and b for simple gases.

The second virial coefficient for a van der Waals gas is easily found to be

$$B_2^{(VW)}(T) = \left(b - \frac{a}{RT}\right). \tag{2.13}$$

We see that $B_2^{(VW)}(T)$ will be negative at low temperatures and will become positive at high temperatures but does not exhibit the maximum observed in real gases. Thus, the van der Waals equation does not predict all the observed

Table 2.1. Van der Waals Constants for Some Simple Gases [4]

	$a(\text{Pa} \cdot \text{m}^6/\text{mol}^2)$	$b(\text{m}^3/\text{mol})$
H_2	0.02476	0.02661
He	0.003456	0.02370
CO_2	0.3639	0.04267
H_2O	0.5535	0.03049
O_2	0.1378	0.03183
N_2	0.1408	0.03913

features of real gases. However, it describes enough of them to make it a worthwhile equation to study. In subsequent chapters, we will repeatedly use the van der Waals equation to study the thermodynamic properties of interacting fluids.

2.C.4. Solids

Solids have the property that their coefficient of thermal expansion, $\alpha_P = (1/v)(\partial v/\partial T)_P$, and their isothermal compressibility, $\kappa_T = -(1/v)(\partial v/\partial P)_T$, where $v = V/n$ is the molar volume, are very small. Therefore, for solids at fairly low temperature we can expand the molar volume of a solid in a Taylor series about zero temperature and zero pressure value, v_0, and obtain the following equation of state:

$$v = v_0(1 + \alpha_P T - \kappa_T P), \tag{2.14}$$

where T is measured in Kelvins. Typical values [5] of κ_T are of the order of 10^{-10}/Pa or 10^{-5}/atm. For example, for solid Ag (silver) at room temperature, $\kappa_T = 1.3 \times 10^{-10}$/Pa (for $P = 0$ Pa), and for diamond at room temperature, $\kappa_T = 1.6 \times 10^{-10}$/Pa (for $P = 4.0 \times 10^8$ Pa $- 10^{10}$ Pa). Typical values of α_P are of the order 10^{-4}/K. For example, for solid Na (sodium) at room temperature we have $\alpha_P = 2 \times 10^{-4}$/K, and for solid K (potassium) we have $\alpha_P = 2 \times 10^{-4}$/K.

2.C.5. Elastic Wire or Rod

For a stretched wire or rod in the elastic limit, Hook's law applies and we can write

$$J = A(T)(L - L_0), \tag{2.15}$$

where J is the tension measured in Newtons per meter, $A(T)$ is temperature dependent coefficient, L is the length of the stretched wire or rod, and L_0 is the

length of the wire when $J = 0$. The coefficient, $A(T)$, may be written $A(T) = A_0 + A_1 T$, where A_0 and A_1 are constants. The constant, A_1, is negative for most substances but may be positive for some substances (including rubber).

2.C.6. Surface Tension [6]

Pure liquids in equilibrium with their vapor phase have a well-defined surface layer at the interface between the liquid and vapor phases. The mechanical properties of the surface layer can be described by thermodynamic state variables. The origin of the surface layer is the unequal distribution of intermolecular forces acting on the molecules at the surface. Molecules in the interior of the liquid are surrounded by, and interact with, molecules on all sides. Molecules at the surface interact primarily with molecules in the liquid, since the vapor phase (away from the critical point) is far less dense than the liquid. As a result, there is a strong tendency for the molecules at the surface to be pulled back into the liquid and for the surface of the liquid to contract. The molecular forces involved are huge. Because of this tendency for the surface to contract, work must be done to increase the free surface of the liquid. When the surface area is increased, molecules from the interior must be brought to the surface and therefore work must be done against interior molecular forces. The *work per unit area* needed to extend the surface area is called the *surface tension of* the liquid. For most pure liquids, the surface tension does not depend on the area and the equation of state has the form

$$\sigma = \sigma_0 \left(1 - \frac{t}{t'}\right)^n, \tag{2.16}$$

where t is the temperature in degrees Celius, σ_0 is the surface tension at $t = 0°\text{C}$, t' is experimentally determined temperature within a few degrees of the critical temperature, and n is an experimental constant which has a value between one and two.

2.C.7. Electric Polarization [6–8]

When an electric field $\mathbf{E}$ is applied to a dielectric material, the particles composing the dielectric will be distorted and an electric polarization field, $\mathbf{P}$ ($\mathbf{P}$ is the induced electric dipole moment per unit volume), will be set up by the material. The polarization is related to the electric field, $\mathbf{E}$, and the electric displacement, $\mathbf{D}$, by the equation

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \tag{2.17}$$

where ε_0 is the permittivity constant, $\varepsilon_0 = 8.854 \times 10^{-12} \text{C}^2/\text{N} \cdot \text{m}^2$. The electric field, $\mathbf{E}$, has units of Newtons per coulomb (N/C), and the electric displacement and electric polarization have units of coulomb per square meter

(C/m^2). **E** results from both external and surface charges. The magnitude of the polarization field, **P**, will depend on the temperature. A typical equation of state for a homogeneous dielectric is

$$\mathbf{P} = \left(a + \frac{b}{T}\right)\mathbf{E} \tag{2.18}$$

for temperatures not too low. Here a and b are experimental constants and T is temperature in degrees Kelvin.

2.C.8. Curie's Law [6–8]

If we consider a paramagnetic solid at constant pressure, the volume changes very little as a function of temperature. We can then specify the state in terms of applied magnetic field and induced magnetization. When the external field is applied, the spins line up to produce a magnetization **M** (magnetic moment per unit volume). The magnetic induction field, **B** (measured in units of teslas, 1 T=1 weber/m^2), the magnetic field strength, **H** (measured in units of amphere/meter), and the magnetization are related through the equation

$$\mathbf{B} = \mu_0\mathbf{H} + \mu_0\mathbf{M}, \tag{2.19}$$

where μ_0 is the permeability constant ($\mu_0 = 4\pi \times 10^{-7}$ T · m/A). The equation of state for such a system at room temperature is well approximated by Curie's law:

$$M = \frac{nD}{T}\mathbf{H}, \tag{2.20}$$

where n is the number of moles, D is an experimental constant dependent on the type of material used, and the temperature, T, is measured in Kelvins.

2.D. THE LAWS OF THERMODYNAMICS [6]

Thermodynamics is based upon four laws. Before we can discuss these laws in a meaningful way, it is helpful to introduce some basic concepts.

A system is in *thermodynamic equilibrium* if the mechanical variables do not change in time and if there are no macroscopic flow processes present. Two systems are separated by a fixed *insulating wall* (a wall that prevents transfer of matter heat and mechanical work between the systems) if the thermodynamic state variables of one can be changed arbitrarily without causing changes in the thermodynamic state variables of the other. Two systems are separated by a *conducting wall* if arbitrary changes in the state variables of one cause changes in the state variables of the other. A conducting wall allows transfer of heat. An insulating wall prevents transfer of heat.

It is useful to distinguish among three types of thermodynamic systems. An *isolated system* is one which is surrounded by an insulating wall, so that no heat or matter can be exchanged with the surrounding medium. A *closed system* is one which is surrounded by a conducting wall so that heat can be exchanged but matter cannot. An *open system* is one which allows both heat and matter exchange with the surrounding medium.

It is possible to change from one equilibrium state to another. Such changes can occur reversibly or irreversibly. A reversible change is one for which the system remains infinitesimally close to the thermodynamic equilibrium—that is, is performed quasi-statically. Such changes can always be reversed and the system brought back to its original thermodynamic state without causing any changes in the thermodynamic state of the universe. For each step of a reversible process, the state variables have a well-defined meaning.

An irreversible or spontaneous change from one equilibrium state to another is one in which the system does not stay infinitesimally close to equilibrium during each step. Such changes often occur rapidly and give rise to flows and "friction" effects. After an irreversible change the system cannot be brought back to its original thermodynamic state without causing a change in the thermodynamic state of the universe. With these ideas in mind, we an now discuss the four laws of thermodynamics.

2.D.1. Zeroth Law: Two Bodies, Each in Thermodynamic Equilibrium with a Third System, are in Thermodynamic Equilibrium with Each Other

The zeroth law is of fundamental importance to experimental thermodynamics because it enables us to introduce the concept of a thermometer and to measure temperatures of various systems in a reproducible manner. If we place a thermometer in contact with a given reference system, such as water at the triple point (where ice, water, and vapor coexist), then the mechanical variables describing the thermodynamic state of the thermometer (e.g., the height of a mercury column, the resistance of a resistor, or the pressure of a fixed volume container of gas) always take on the same values. If we then place the thermometer in contact with a third system and the mechanical variables do not change, then we say that the third system, the thermometer, and water at the triple point all have the same "temperature." Changes in the mechanical variables of the thermometer as it is cooled or heated are used as a measure of temperature change.

2.D.2. First Law: Energy Is Conserved

The first law tells us that there is a store of energy in the system, called the internal energy, U, which can be changed by causing the system to do work, $đW$, or by adding heat, $đQ$, to the system. We use the notation, $đW$, to indicate that the differential is not exact.) The change in the internal energy which

results from these two processes is given by

$$dU = đQ - đW. \tag{2.21}$$

The work, $đW$, may be due to changes in any relevant extensive "mechanical" or chemical variable. In general it can be written

$$đW = PdV - JdL - \sigma dA - \mathbf{E} \cdot d\mathbf{P} - \mathbf{H} \cdot d\mathbf{M} - \phi de - \sum_j \mu_j' dN_j, \tag{2.22}$$

where $dU, dV, dL, dA, d\mathbf{P}, d\mathbf{M}, de$, and dN_j are exact differentials, but $đQ$ and $đW$ are not because they depend on the path taken (on the way in which heat is added or work is done). The meaning of the first five terms in Eq. (2.22) was discussed in Section (2.C). The term, $-\phi de$, is the work the system needs to do it is has an electric potential, ϕ, and increases its charge by an amount, de. The last term, $-\mu_j' dN_j$, is the chemical work required for the system to add dN_j neutral particles if it has chemical potential, μ_j'. We may think of $-P, J, \sigma, \mathbf{E}, \mathbf{H}, \phi$, and μ_j' as generalized forces, and we may think of $dV, dL, dA, d\mathbf{P}, \mathrm{d}\mathbf{M}, de$ and dN_j as generalized displacements.

It is useful to introduce a generalized mechanical force, Y, which denotes quantities such as, $-P, J, \sigma, \mathbf{E}, \mathbf{H}$, and ϕ , and a generalized displacement, X, which denotes the corresponding displacements, $V, L, A, \mathbf{P}, \mathbf{M}$, and e, respectively. Then the first law can be written in the form

$$dU = đQ + YdX + \sum_j \mu_j' dN_j. \tag{2.23}$$

Note that μ_j' is a chemical force and dN_j is a chemical displacement. Note also that the pressure, P, has a different sign from the other generalized forces. If we increase the pressure, the volume increases, whereas if we increase the force, Y, for all other cases, the extensive variable, X, decreases.

2.D.3. Second Law: Heat Flows Spontaneously from High Temperatures to Low Temperatures

There are a number of ways to state the second law, with the one given above being the simplest. Three alternative versions are [6]:

(a) *The spontaneous tendency of a system to go toward thermodynamic equilibrium cannot be reversed without at the same time changing some organized energy, work, into disorganized energy, heat.*

(b) *In a cyclic process, it is not possible to convert heat from a hot reservoir into work without at the same time transferring some heat to a colder reservoir.*

(c) *The entropy change of any system and its surroundings, considered together, is positive and approaches zero for any process which approaches reversibility.*

The second law is of immense importance from many points of view. From it we can compute the maximum possible efficiency of an engine which transforms heat into work. It also enables us to introduce a new state variable, the entropy, S, which is conjugate to the temperature. The entropy gives us a measure of the degree of disorder in a sysem and also gives us a means for determining the stability of equilibrium states, and, in general, it forms an important link between reversible and irreversible processes.

The second law is most easily discussed in terms of an ideal heat engine first introduced by Carnot. The construction of all heat engines is based on the observation that if heat is allowed to flow from a high temperature to a lower temperature, part of the heat can be turned into work. Carnot observed that temperature differences can disappear spontaneously without producing work. Therefore, he proposed a very simple heat engine consisting only of reversible steps, thereby eliminating wasteful heat flows. The Carnot engine consists of the four steps shown in Fig. 2.2. These include:

(a) Isothermal (constant temperature) absorption of heat ΔQ_{12} from a reservoir at a high temperature τ_h (we use Δ to indicate a finite rather than an infinitesimal amount of heat) (the process $1 \rightarrow 2$).

(b) Adiabatic (constant heat content) change in temperature from τ_h to the lower value τ_c (the process $2 \rightarrow 3$).

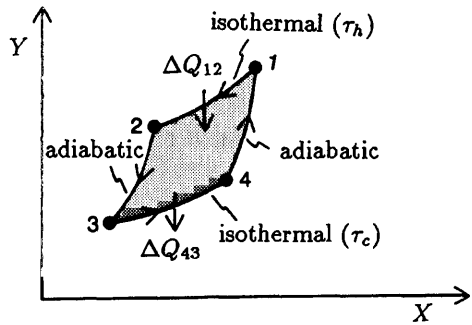


Fig. 2.2. A Carnot engine which runs on a substance with state variables, X and Y. The processes $1 \rightarrow 2$ and $3 \rightarrow 4$ occur isothermally at temperatures τ_h and τ_c, respectively. The processes $2 \rightarrow 3$ and $4 \rightarrow 1$ occur adiabatically. The heat absorbed is ΔQ_{12} and the heat ejected is ΔQ_{43}. The shaded area is equal to the work done during the cycle. The whole process takes place reversibly.

(**c**) Isothermal expulsion of heat ΔQ_{43} into a reservoir at temperature τ_c (the process $3 \rightarrow 4$).

(**d**) Adiabatic return to the initial state at temperature τ_h (the process $4 \rightarrow 1$).

The work done by the engine during one complete cycle can be found by integrating the differential element of work $Y\,dX$ about the entire cycle. We see that the total work ΔW_{tot} done by the engine is given by the shaded area in Fig. 2.2.

The total efficiency η of the heat engine is given by the ratio of the work done to heat absorbed:

$$\eta = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}} \tag{2.24}$$

Since the internal energy U is state variable and independent of path, the total change ΔU_{tot} for one complete cycle must be zero. The first law then enables us to write

$$\Delta U_{\text{tot}} = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} = 0 \tag{2.25}$$

and thus

$$\Delta W_{\text{tot}} = \Delta Q_{\text{tot}} = \Delta Q_{12} + \Delta Q_{34} = \Delta Q_{12} - \Delta Q_{43}. \tag{2.26}$$

If we combine Eqs. (2.24) and (2.26), we can write the efficiency in the form

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} \tag{2.27}$$

A 100% efficient engine is one which converts all the heat it absorbs into work. However, as we shall see, no such engine can exist in nature.

The great beauty and utility of the Carnot engine lies in the fact that it is the most efficient of all heat engines operating between two heat reservoirs, each at a (different) fixed temperature. This is a consequence of the second law. To prove this let us consider two heat engines, A and B (cf. Fig. 2.3), which run between the same two reservoirs τ_h and τ_c. Let us assume that engine A is a heat engine with irreversible elements and B is a reversible Carnot engine. We will adjust the mechanical variables X and Y so that during one cycle both engines perform the same amount of work (note that X_{A} and Y_{A} need not be the same mechanical variables as X_{B} and Y_{B}):

$$\Delta W_{\text{tot}}^{\text{A}} = \Delta W_{\text{tot}}^{\text{B}} \equiv \Delta W. \tag{2.28}$$

Let us now assume that engine A is more efficient than engine B:

$$\eta_{\text{A}} > \eta_{\text{B}} \tag{2.29}$$

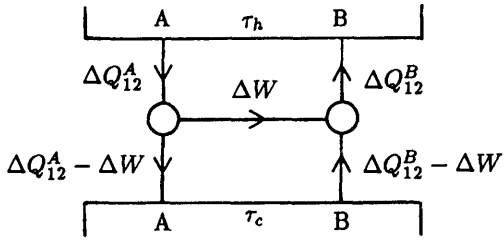


Fig. 2.3. Two heat engines, A and B, work together. Engine B acts as a heat pump while engine A acts as a heat engine with irreversible elements. Engine A cannot have a greater efficiency than engine B without violating the second law.

and thus

$$\frac{\Delta W}{\Delta Q_{12}^{\mathrm{A}}} > \frac{\Delta W}{\Delta Q_{12}^{\mathrm{B}}} \tag{2.30}$$

or

$$\Delta Q_{12}^{\mathrm{B}} > \Delta Q_{12}^{\mathrm{A}}. \tag{2.31}$$

We can use the work produced by engine A to drive the Carnot engine as a refrigerator. Since the Carnot engine is reversible, it will have the same efficiency whether it runs as a heat engine or as a heat pump. The work, ΔW, produced by A will be used to enable the Carnot engine B to pump heat from the low-temperature reservoir to the high-temperature reservoir. The net heat extracted from reservoir τ_c and delivered to reservoir τ_h is

$$\Delta Q_{12}^{\mathrm{B}} - \Delta W - (\Delta Q_{12}^{\mathrm{A}} - \Delta W) = \Delta Q_{12}^{\mathrm{B}} - \Delta Q_{12}^{\mathrm{A}}. \tag{2.32}$$

If engine A is more efficient than engine B, then the combined system has caused heat to flow from low temperature to high temperature without any work being expended by an outside source. This violates the second law and therefore engine A cannot be more efficient than the Carnot engine. If we now assume that both engines are Carnot engines, we can show, by similar arguments, that they both must have the same efficiency. Thus, we reach the following conclusion: *No engine can be more efficient than a Carnot engine, and all Carnot engines have the same efficiency.*

From the above discussion, we see that the efficiency of a Carnot engine is completely independent of the choice of mechanical variables X and Y and therefore can only depend on the temperatures τ_h and τ_c of the two reservoirs. This enables us to define an absolute temperature scale. From Eq. (2.27) we see that

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(\tau_h, \tau_c), \tag{2.33}$$

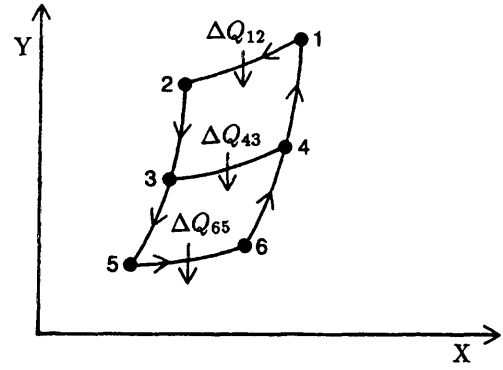


Fig. 2.4. Two Carnot engines running between three reservoirs with temperatures $\tau_h > \tau > \tau_c$ have the same overall efficiency as one Carnot engine running between reservoirs with temperatures $\tau_h > \tau c$.

where $f(\tau_h, \tau_c)$ is some function of temperatures τ_h and τ_c. The function $f(\tau_h, \tau_c)$ has a very special form. Let us consider two heat engines running between three reservoirs $\tau_h > \tau' > \tau_c$ (cf. Fig. 2.4). We can write

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(\tau_h, \tau'), \tag{2.34}$$

$$\frac{\Delta Q_{65}}{\Delta Q_{43}} = f(\tau', \tau_c), \tag{2.35}$$

and

$$\frac{\Delta Q_{65}}{\Delta Q_{12}} = f(\tau_h, \tau_c), \tag{2.36}$$

so that

$$f(\tau_h, \tau_c) = f(\tau_h, \tau')f(\tau', \tau_c). \tag{2.37}$$

Thus, $f(\tau_h, \tau_c) = g(\tau_h)g^{-1}(\tau_c)$ where $g(\tau)$ is some function of temperature.

One of the first temperature scales proposed but not widely used is due to W. Thomson (Lord Kelvin) and is called the *Thomson scale* [9]. It has the form

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{e^{\tau_c^\circ}}{e^{\tau_h^\circ}} \tag{2.38}$$

The Thomson scale is defined so that a given unit of heat ΔQ_{12} flowing between temperatures $\tau^\circ \to (\tau^\circ - 1)$ always produces the same amount of work, regardless of the value of τ°.

A more practical scale, the Kelvin scale, was also introduced by Thomson. It is defined as

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{\tau_c}{\tau_h}. \tag{2.39}$$

As we will see below, the Kelvin scale is identical to the temperature used in the ideal gas equation of state and is the temperature measured by a gas thermometer. For this reason, the Kelvin scale is the internationally accepted temperature scale at the present time.

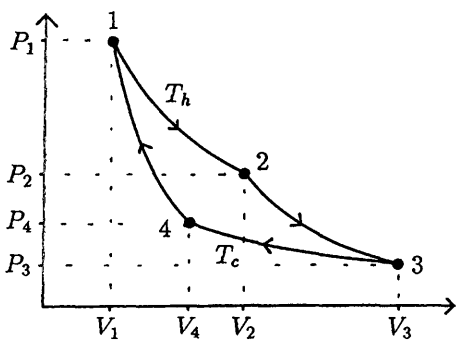
The units of degrees Kelvin are the same as degrees Celsius. The ice point of water at atmospheric pressure is defined as 0 °C, and the boiling point is defined as 100 °C. The triple point of water is 0.01 °C. To obtain a relation between degrees Kelvin and degrees Celsius, we can measure pressure of a real *dilute* gas as a function of temperature at fixed volume. It is found experimentally that the pressure varies linearly with temperature and goes to zero at $t_c = -273.15\,^{\circ}\mathrm{C}$. Thus, from the ideal gas law, we see that degrees Kelvin, T, are related to degrees Celsius, t_c, by the equation

$$T = (t_c + 273.15). \tag{2.40}$$

The triple point of water is fixed at $T = 273.16$ K.

In Exercise 2.2, we compute the efficiency of a Carnot engine which uses an ideal gas as an operating substance. However, Carnot engines can be constructed using any of a variety of substances (some examples are left as problems). Regardless of the operating substance, all Carnot engines have the same efficiency.

■ **Exercise 2.2.** Compute the efficiency of a Carnot cycle (shown in the figure below) which uses a monatomic ideal gas as an operating substance.



Answer: The equation of state of an ideal gas is $PV = nRT$, where $P = -Y$ is the pressure and $V = X$ is the volume, T is the temperature in Kelvins, and n is the number of moles. The internal energy is $U = (3/2)nRT$. The Carnot

cycle for an ideal gas is shown in the figure below. The part $1 \rightarrow 2$ is an isothermal expansion of the system, and the path $3 \rightarrow 4$ is an isothermal contraction. It is clear from the equation of state that the temperature, T_h, of path $1 \rightarrow 2$ is higher than the temperature, T_c, of path $3 \rightarrow 4$. The path $2 \rightarrow 3$ is an adiabatic expansion of the system, and the path $4 \rightarrow 1$ is an adiabatic contraction. We shall assume that n is constant during each cycle.

Let us first consider the isothermal paths. Since the temperature is constant along these paths, $dU = \frac{3}{2}nRdT = 0$. Thus, along the path $1 \rightarrow 2, \not{d}Q = \not{d}W = nRT_h(dV/V)$. The heat absorbed along the path $1 \rightarrow 2$ is

$$\Delta Q_{12} = nRT_h \int_{V_1}^{V_2} \frac{dV}{V} = nRT_h \ln\left(\frac{V_2}{V_1}\right). \tag{1}$$

The heat absorbed along the path $3 \rightarrow 4$ is

$$\Delta Q_{34} = nRT_c \ln\left(\frac{V_4}{V_3}\right). \tag{2}$$

Since $V_2 > V_1, \Delta Q_{12} > 0$ and heat is absorbed along the path $1 \rightarrow 2$. Since $V_3 > V_4$, $\Delta Q_{34} < 0$ and heat is ejected along the path $3 \rightarrow 4$.

Let us next consider the adiabatic paths. Along the adiabatic path, $\not{d}Q = 0 = dU + PdV = (3/2)nRdT + PdV$. If we make use of the equation of state, we find $(3/2)(dT/T) = -(dV/V)$. We now integrate to find $T^{3/2}V =$ constant for an adiabatic process. Thus, along the paths $2 \rightarrow 3$ and $4 \rightarrow 1$, respectively, we have

$$T_c V_3^{2/3} = T_h V_2^{2/3} \quad \text{and} \quad T_c V_4^{2/3} = T_h V_1^{2/3}. \tag{3}$$

For the entire cycle, we can write $\Delta U_{\text{tot}} = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} = 0$. Thus $\Delta W_{\text{tot}} = \Delta Q_{\text{tot}} = \Delta Q_{12} + \Delta Q_{34}$. The efficiency of the Carnot cycle is

$$\eta = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}} = 1 + \frac{\Delta Q_{34}}{\Delta Q_{12}} = 1 - \frac{T_c}{T_h}\frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} = 1 - \frac{T_c}{T_h}, \tag{4}$$

since from Eq. (3) we have

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}.$$

We can use the Carnot engine to define a new state variable called the *entropy*. All Carnot engines have an efficiency

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} = 1 - \frac{T_c}{T_h}. \tag{2.41}$$

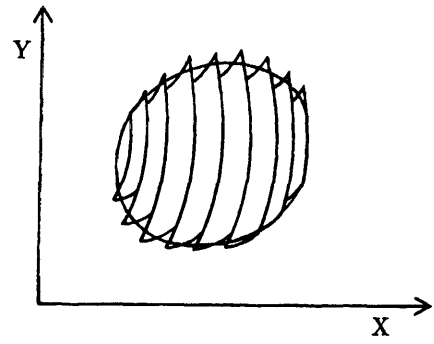


Fig. 2.5. An arbitrary reversible heat engine is composed of many infinitesimal Carnot engines. The area enclosed by the curve is equal to the work done by the heat engine.

(cf. Exercise 2.2) regardless of operating substance. Using Eq. (2.41), we can write the following relation for a Carnot cycle:

$$\frac{\Delta Q_{12}}{T_h} + \frac{\Delta Q_{34}}{T_c} = 0. \tag{2.42}$$

(note the change in indices in ΔQ_{34}). Equation (2.42) can be generalized to the case of an arbitrary *reversible* heat engine because we can consider such an engine as being composed of a sum of many infinitesimal Carnot cycles (cf. Fig. 2.5). Thus, for an arbitrary reversible heat engine we have

$$\oint \frac{đQ}{T} = 0. \tag{2.43}$$

The quantity

$$dS \equiv \frac{đQ}{T} \tag{2.44}$$

is an exact differential and the quantity S, called the *entropy*, may be considered a new state variable since the integral of dS about a closed path gives zero.

No heat engine can be more efficient than a Carnot engine. Thus, an engine which runs between the same two reservoirs but contains spontaneous or irreversible processes in some part of the cycle will have a lower efficiency, and we can write

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} > \frac{T_c}{T_h} \tag{2.45}$$

and

$$\frac{\Delta Q_{12}}{T_h} - \frac{\Delta Q_{43}}{T_c} < 0. \tag{2.46}$$

For an arbitrary heat engine which contains an irreversible part, Eq. (2.46) gives

the very important relation

$$\oint \frac{đQ}{T} < 0. \tag{2.47}$$

For an irreversible process, $đQ/T$ can no longer be considered an exact differential.

A system may evolve between two thermodynamic states either by a reversible path or by a spontaneous, irreversible path. For any process, reversible or irreversible, the entropy change depends only on the initial and final thermodynamic states of the system, since the entropy is a state variable. If the system evolves between the initial and final states via a reversible path, then we can compute the entropy change along that path. However, if the system evolves between the initial and final states via an irreversible path, then we must construct a hypothetical reversible path between the initial and final states in order to use the equations of thermodynamics to compute the entropy change during the spontaneous process. For the irreversible path, the heat absorbed by the system will be less than that along the reversible path [cf. Eqs. (2.45)–(2.47)]. Therefore, $\int_{\text{irrev}} đQ/T < \int_{\text{rev}} đQ/T$. This means that *for an irreversible process, $\int_{\text{irrev}} đQ/T$ does not contain all contributions to the entropy change.* Some of it comes from the disorder created by spontaneity. This result is usually written in the form

$$dS = \frac{đQ}{T} + d_iS, \tag{2.48}$$

where d_iS denotes the *entropy production* due to spontaneous processes. For a reversible process, $d_iS = 0$ and $dS = (1/T)đQ$ so the entropy change is entirely due to a flow of heat into or out of the system. For a spontaneous (irreversible)) process, $d_iS > 0$.

For an isolated system we have $đQ = 0$, and we obtain the important relation

$$dS = d_iS \geq 0, \tag{2.49}$$

where the equality holds for a reversible process and the inequality holds for a spontaneous or irreversible process. Since the equilibrium state is, by definition, a state which is stable against spontaneous changes, Eq. (2.49) tells us that the equilibrium state is a state of maximum entropy. As we shall see, this fact gives an important criterion for determining the stability of the equilibrium state for an isolated system.

2.D.4. Third Law: The Difference in Entropy Between States Connected by a Reversible Process Goes to Zero in the Limit $T \to 0$ K [9–11]

The third law was first proposed by Nernst in 1906 on the basis of experimental observations and is a consequence of quantum mechanics. Roughly speaking, a

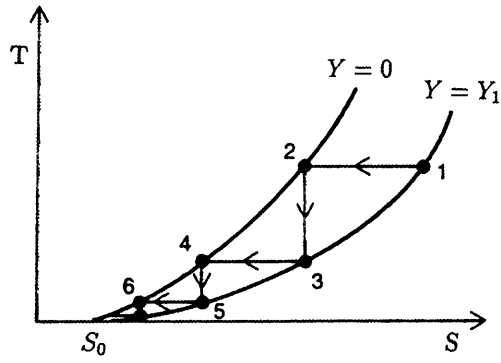


Fig. 2.6. The fact that curves $Y = 0$ and $Y = Y_1$ must approach the same point (the third law) makes it impossible to reach absolute zero by a finite number of reversible steps.

system at zero temperature drops into its lowest quantum state and in this sense becomes completely ordered. If entropy can be thought of as a measure of disorder, then at $T = 0$ K it must take its lowest value.

An alternative statement of the third law, and a direct consequence of the above statement, is, *It is impossible to reach absolute zero in a finite number of steps if a reversible process is used.* This alternative statement is easily demonstrated by means of a plot in the S–T plane. In Fig. 2.6 we have plotted the curves as a function of S and T for two states $Y = 0$ and $Y = Y_1$ for an arbitrary system. (A specific example might be a paramagnetic salt with $Y = H$.) We can cool the system by alternating between the two states, adiabatically and isothermally. From Eqs. (2.5) and (2.6), we write

$$\left(\frac{\partial T}{\partial Y}\right)_{S,N} = -\left(\frac{\partial T}{\partial S}\right)_{Y,N} \cdot \left(\frac{\partial S}{\partial Y}\right)_{T,N}. \tag{2.50}$$

As we shall show in Section 2.H, thermal stability requires that $(\partial S/\partial T)_Y \geq 0$. Equation (2.50) tells us that if T decreases as Y increases isentropically, then S must decrease as Y decreases isothermally, as shown in Fig. 2.6. For the process $1 \rightarrow 2$ we change from state $Y = Y_1$ to state $Y = 0$ isothermally, thus squeezing out heat, and the entropy decreases. For process $2 \rightarrow 3$, we increase Y adiabatically from $Y = 0$ to $Y = Y_1$ and thus decrease the temperature. We can repeat these processes as many times as we wish. However, as we approach $T = 0$ K, we know by the third law that the two curves must approach the same point and must therefore begin to approach each other, thus making it impossible to reach $T = 0$ K in a finite number of steps.

Another consequence of the third law is that certain derivatives of the entropy must approach zero as $T \rightarrow 0$ K. Let us consider a process at $T = 0$ K such that $Y \rightarrow Y + dY$ and $X \rightarrow X + dX$. Then the change in entropy if Y, T, and

N are chosen as independent variables is (assume $dN = 0$)

$$dS = \left(\frac{\partial S}{\partial Y}\right)_{N,T=0} dY, \tag{2.51}$$

or if X, T, and N are chosen as independent we obtain

$$dS = \left(\frac{\partial S}{\partial X}\right)_{N,T=0} dX. \tag{2.52}$$

Thus, if the states $(Y, T = 0\,\mathrm{K})$ and $(Y + dY, T = 0\,\mathrm{K})$ or the states $(X, T = 0\,\mathrm{K})$ and $(X + dX, T = 0\,\mathrm{K})$ are connected by a reversible process, we must have $dS = 0$ (third law) and therefore

$$\left(\frac{\partial S}{\partial Y}\right)_{N,T=0} = 0 \tag{2.53}$$

and

$$\left(\frac{\partial S}{\partial X}\right)_{N,T=0} = 0 \tag{2.54}$$

Equations (2.53) and (2.54) appear to be satisfied by real substances.

2.E. FUNDAMENTAL EQUATION OF THERMODYNAMICS [10]

The entropy plays a central role in both equilibrium and nonequilibrium thermodynamics. It can be thought of as a measure of the disorder in a system. As we shall see in Chapter 7, entropy is obtained microscopically by state counting. The entropy of an isolated system is proportional to the logarithm of the number of states available to the system. Thus, for example, a quantum system in a definite quantum state (pure state) has zero entropy. However, if the same system has finite probability of being in any of a number of quantum states, its entropy will be nonzero and may be quite large.

The entropy is an extensive, additive quantity. If a system is composed of a number of independent subsystems, then the entropy of the whole system will be the sum of the entropies of the subsystems. This additive property of the entropy is expressed mathematically by the relation

$$S(\lambda U, \lambda X, \{\lambda N_i\}) = \lambda S(U, X, \{N_i\}). \tag{2.55}$$

That is, the entropy is a first-order homogeneous function of the extensive state variables of the system. If we increase *all* the extensive state variables by a factor λ, then the entropy must also increase by a factor λ.

Differential changes in the entropy are related to differential changes in the extensive state variables through the combined first and second laws of thermodynamics:

$$TdS \geq \not{d}Q = dU - YdX - \sum_j \mu_j' dN_j. \tag{2.56}$$

The equality holds if changes in the thermodynamic state are reversible. The inequality holds if they are spontaneous or irreversible. Equations (2.55) and (2.56) now enable us to define the Fundamental Equation of thermodynamics. Let us take the derivative of λS with respect to λ:

$$\begin{aligned}\frac{d}{d\lambda}(\lambda S) = &\left(\frac{\partial S}{\partial \lambda U}\right)_{X,\{N_j\}} \frac{d}{d\lambda}(\lambda U) + \left(\frac{\partial S}{\partial \lambda X}\right)_{U,\{N_j\}} \frac{d}{d\lambda}(\lambda X) \\ &+ \sum_j \left(\frac{\partial S}{\partial \lambda N_j}\right)_{U,X,\{N_{i\neq j}\}} \frac{d(\lambda N_j)}{d\lambda}.\end{aligned} \tag{2.57}$$

However, from Eq. (2.56) we see that

$$\left(\frac{\partial S}{\partial U}\right)_{X,\{N_j\}} = \frac{1}{T}, \tag{2.58}$$

$$\left(\frac{\partial S}{\partial X}\right)_{U,\{N_j\}} = -\frac{Y}{T}, \tag{2.59}$$

and

$$\left(\frac{\partial S}{\partial N_j}\right)_{U,X,\{N_{i\neq j}\}} = -\frac{\mu_j'}{T}. \tag{2.60}$$

Equations (2.58)–(2.60) are called the thermal, mechanical, and chemical *equations of state*, respectively. The mechanical equation of state, Eq. (2.59), is the one most commonly seen and is the one which is described in Section 2.C. If we now combine Eqs (2.57)–(2.60), we obtain

$$TS = U - XY - \sum_j \mu_j' N_j. \tag{2.61}$$

Equation (2.61) is called the *Fundamental Equation of thermodynamics* (it is also known as *Euler's equation*) because it contains all possible thermodynamic information about the thermodynamic system. If we take the differential of Eq. (2.61) and subtract Eq. (2.56) (we will take the reversible case), we obtain

another important equation,

$$SdT + XdY + \sum_j N_j d\mu'_j = 0, \tag{2.62}$$

which is called the *Gibbs–Duhem* equation. The Gibbs–Duhem equation relates differentials of intensive state variables.

For a monatomic system, the above equations simplify somewhat if we work with densities. As a change of pace, let us work with molar densities. For single component system the Fundamental Equation can be written $TS = U - YX - \mu n$ and the combined first and second laws (for reversible processes) can be written $TdS = dU - YdX - \mu dn$. Let us now introduce the molar entropy, $s = S/n$, the molar density, $x = X/n$, and the molar internal energy, $u = U/n$. Then the Fundamental Equation becomes

$$Ts = u - Yx - \mu, \tag{2.63}$$

and the combined first and second laws become (for reversible processes)

$$Tds = du - Ydx. \tag{2.64}$$

Therefore, $(\partial s/\partial u)_x = 1/T$ and $(\partial s/\partial x)_u = -Y/T$. The Gibbs–Duhem equation is simply

$$d\mu = -sdT - xdY, \tag{2.65}$$

and therefore the chemical potential has the form, $\mu = \mu(T, Y)$, and is a function only of the intensive variables, T and Y. Note also that $s = -(\partial\mu/\partial T)_Y$ and $x = -(\partial\mu/\partial Y)_T$. In Exercise 2.3, we use these equations to write the Fundamental Equation for an ideal monatomic gas.

■ **EXERCISE 2.3.** The entropy of n moles of a monatomic ideal gas is $S = (5/2)nR + nR\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$, where V_0, n_0, and T_0 are constants (this is called the *Sackur–Tetrode equation*). The mechanical equation of state is $PV = nRT$. (a) Compute the internal energy. (b) Compute the chemical potential. (c) Write the Fundamental Equation for an ideal monatomic ideal gas and show that it is a first-order homogeneous function of the extensive state variables.

Answer: It is easiest to work in terms of densities. The molar entropy can be written $s = (5/2)R + R\ln[(v/v_0)(T/T_0)^{3/2}]$ ($v = V/n$ is the molar volume), and the mechanical equation of state is $Pv = RT$.

(a) The combined first and second law gives $du = Tds - Pdv$. If we further note that $ds = (\partial s/\partial T)_v dT + (\partial s/\partial v)_T dv$, then

$$du = T\left(\frac{\partial s}{\partial T}\right)_v dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - P\right]dv = \frac{3}{2}RdT, \tag{1}$$

since $(\partial s/\partial T)_v = (3R/2T)$ and $(\partial s/\partial v)_T = R/v$. Therefore, the molar internal energy is $u = \frac{3}{2}RT + u_0$ where u_0 is a constant, and the total internal energy is $U = nu = \frac{3}{2}nRT + U_0$, where $U_0 = nu_0$.

(b) Let us rewrite the molar entropy in terms of pressure instead of molar volume. From the mechanical equation of state, $v = (RT/P)$ and $v_0 = (RT_0/P_0)$. Therefore, $s = \frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}]$. From the Gibbs–Duhem equation, $(\partial\mu/\partial T)_P = -s = -(\frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}])$ and $(\partial\mu/\partial P)_T = v = RT/P$. If we integrate these we obtain the following expression for the molar chemical potential:

$$\mu = -RT\ln\left[\frac{P_0}{P}\left(\frac{T}{T_0}\right)^{5/2}\right]. \tag{2}$$

(c) Let us rewrite the entropy in terms of the internal energy, volume, and number of moles. We obtain

$$S = \frac{5}{2}nR + nR\ln\left[\frac{V}{V_0}\left(\frac{n_0}{n}\right)^{5/2}\left(\frac{U}{U_0}\right)^{3/2}\right]. \tag{3}$$

Equation (3) is the Fundamental Equation for an ideal monatomic gas. It clearly is a first-order homogeneous function of the extensive variables.

It is interesting to note that this classical ideal gas does not obey the third law of thermodynamics and cannot be used to describe systems at very low temperatures. At very low temperatures we must include quantum corrections to the ideal gas equation of state.

2.F. THERMODYNAMIC POTENTIALS [11]

In conservative mechanical systems, such as a spring or a mass raised in a gravitational field, work can be stored in the form of potential energy and subsequently retrieved. *Under certain circumstances* the same is true for thermodynamic systems. We can store energy in a thermodynamic system by doing work on it through a reversible process, and we can eventually retrieve that energy in the form of work. The energy which is stored and retrievable in the form of work is called the *free energy*. There are as many different forms of free energy in a thermodynamic system as there are combinations of

constraints. In this section, we shall discuss the five most common ones: internal energy, U; the enthalpy, H; the Helmholtz free energy, A; the Gibbs free energy, G; and the grand potential, Ω. These quantities play a role analogous to that of the potential energy in a spring, and for that reason they are also called the *thermodynamic potentials*.

2.F.1. Internal Energy

From Eq. (2.61) the fundamental equation for the internal energy can be written

$$U = ST + YX + \sum_j \mu_j' N_j, \tag{2.66}$$

where T, Y, and μ_j' are considered to be functions of S, X, and $\{N_j\}$ [cf. Eqs. (2.58)–(2.60)]. From Eq. (2.56), the total differential of the internal energy can be written

$$dU \leq TdS + YdX + \sum_j \mu_j' dN_j. \tag{2.67}$$

The equality holds for reversible changes, and the inequality holds for changes which are spontaneous. From Eq. (2.67) we see that

$$T = \left(\frac{\partial U}{\partial S}\right)_{X,\{N_j\}}, \tag{2.68}$$

$$Y = \left(\frac{\partial U}{\partial X}\right)_{S,\{N_j\}}, \tag{2.69}$$

and

$$\mu_j' = \left(\frac{\partial U}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}}. \tag{2.70}$$

We can use the fact that dU is an exact differential to find relations between derivatives of the intensive variables, T, Y, and μ_j'. From Eq. (2.4) we know, for example, that

$$\left[\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial S}\right)_{X,\{N_j\}}\right]_{S,\{N_j\}} = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial X}\right)_{S,\{N_j\}}\right]_{X,\{N_j\}}. \tag{2.71}$$

From Eqs. (2.68), (2.69), and (2.71), we obtain

$$\left(\frac{\partial T}{\partial X}\right)_{S,\{N_j\}} = \left(\frac{\partial Y}{\partial S}\right)_{X,\{N_j\}}. \tag{2.72}$$

$(i+1)$ additional relations like Eq. (2.72) exist and lead to the identities

$$\left(\frac{\partial T}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial S}\right)_{X,\{N_j\}}, \tag{2.73}$$

$$\left(\frac{\partial Y}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial X}\right)_{S,\{N_j\}}, \tag{2.74}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{S,X,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}}. \tag{2.75}$$

Equations (2.72)–(2.75) are extremely important both theoretically and experimentally because they provide a relation between rates of change of seemingly diverse quantities. They are called *Maxwell relations*.

For a substance with a single type of particle, the above equations simplify if we work with densities. Let $u = U/n$ denote the molar internal energy. Then the Fundamental Equation can be written $u = Ts + Yx + \mu$, where s is the molar entropy and x is a molar density. The combined first and second laws (for reversible processes) are $du = Tds + Ydx$. Therefore we obtain the identities $(\partial u/\partial s)_x = T$ and $(\partial u/\partial x)_s = Y$. Maxwell relations reduce to $(\partial T/\partial x)_s = (\partial Y/\partial s)_x$.

The internal energy is a thermodynamic potential or free energy because for processes carried out reversibly in an isolated, closed system at fixed X and $\{N_j\}$, the change in internal energy is equal to the maximum amount of work that can be done on or by the system. As a specific example, let us consider a *PVT* system (cf. Fig. 2.7). We shall enclose a gas in an insulated box with fixed total volume and divide it into two parts by a movable conducting wall. We can do work on the gas or have the gas do work by attaching a mass in a gravitational field to the partition via a pulley and insulated string. To do work reversibly, we assume that the mass is composed of infinitesimal pieces which can be added or removed one by one. If $P_1A + mg > P_2A$, then work is done on the gas by the mass, and if $P_1A + mg < P_2A$, the gas does work on the mass. The first law can be written

$$\Delta U = \Delta Q - \Delta W, \tag{2.76}$$

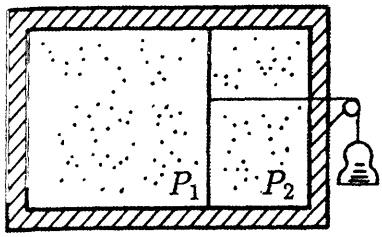


Fig. 2.7. For a reversible process in a closed, insulated box of fixed size ($\Delta S = 0$, $\Delta V = 0$, $\Delta N_j = 0$), the work done in lifting the weight will be equal to the change in the internal energy, $(\Delta U)_{S,V,N} = -\Delta W_{\text{free}}$.

where ΔU is the change in total internal energy of the gas, ΔQ is the heat flow through the walls, and ΔW can be divided into work done due to change in size of the box, $\int P dV$, and work done by the gas in raising the weight, ΔW_{free}:

$$\Delta W = \int P dV + \Delta W_{\text{free}}. \tag{2.77}$$

For a reversible process, $\Delta Q = \int T dS$. For the reversible process pictured in Fig. 2.7, $\Delta Q = 0, \Delta V = 0$, and $\Delta N_j = 0$ (if no chemical reactions take place). Therefore,

$$(\Delta U)_{S,V,\{N_j\}} = -\Delta W_{\text{free}}. \tag{2.78}$$

Thus, *for a reversible process at constant S, V,* and N_j, *work can be stored in the form of internal energy and can be recovered completely.* Under these conditions, internal energy behaves like a potential energy.

For a spontaneous process, work can only be done at constant S, V, and $\{N_i\}$ if we allow heat to leak through the walls. The first and second laws for a spontaneous process take the form

$$\int dU = \Delta U < \int T\, dS - \int P\, dV - \Delta W_{\text{free}} + \sum_j \int \mu_j' dN_j, \tag{2.79}$$

where the integrals are taken over a reversible path between initial and final states and not the actual spontaneous path. We can do work on the gas spontaneously by allowing the mass to drop very fast. Then part of the work goes into stirring up the gas. In order for the process to occur at constant entropy, some heat must leak out since $\Delta Q < \int T\, dS = 0$. Thus, for a spontaneous process

$$(\Delta U)_{S,V,\{N_j\}} < -\Delta W_{\text{free}}. \tag{2.80}$$

Not all work is changed to internal energy and is retrievable. Some is wasted in stirring the gas. (Note that for this process the entropy of the universe has increased since heat has been added to the surrounding medium.)

For processes involving mechanical variables Y and X we can write Eqs. (2.78) and (2.80) in the form

$$(\Delta U)_{S,X,\{N_j\}} \leq (-\Delta W_{\text{free}}), \tag{2.81}$$

where ΔW_{free} is any work done by the system other than that required to change X. *For a reversible process at constant S, X, and $\{N_j\}$, work can be stored as internal energy and can be recovered completely.*

If a process takes place in which no work is done on or by the system, then Eq. (2.81) becomes

$$(\Delta U)_{S,X,\{N_j\}} \leq 0 \tag{2.82}$$

and the internal energy either does not change (reversible process) or decreases (spontaneous process). Since a system in equilibrium cannot change its state spontaneously, we see that *an equilibrium state at fixed S, X,* and $\{N_j\}$ *is a state of minimum internal energy.*

2.F.2. Enthalpy

The internal energy is the convenient potential to use for processes carried out at constant X, S, and $\{N_j\}$. However, it often happens that we wish to study the thermodynamics of processes which occur at constant S, Y, and $\{N_j\}$. Then it is more convenient to use the enthalpy.

The enthalpy, H, is useful for systems which are thermally isolated and closed but mechanically coupled to the outside world. It is obtained by adding to the internal energy an additional energy due to the mechanical coupling:

$$H \equiv U - XY = ST + \sum_j \mu_j' N_j. \tag{2.83}$$

The addition of the term $-XY$ has the effect of changing the independent variables from (S, X, N_j) to (S, Y, N_j) and is called a *Legendre transformation.* If we take the differential of Eq. (2.83) and combine it with Eq. (2.67), we obtain

$$dH \leq T\,dS - X\,dY + \sum_j \mu_j' dN_j \tag{2.84}$$

and, therefore,

$$T = \left(\frac{\partial H}{\partial S}\right)_{Y,\{N_j\}}, \tag{2.85}$$

$$X = -\left(\frac{\partial H}{\partial Y}\right)_{S,\{N_j\}}, \tag{2.86}$$

and

$$\mu_j' = \left(\frac{\partial H}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}}. \tag{2.87}$$

Since dH is an exact differential, we can use Eq. (2.4) to obtain a new set of Maxwell relations:

$$\left(\frac{\partial T}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial X}{\partial S}\right)_{Y,\{N_j\}}, \tag{2.88}$$

$$\left(\frac{\partial T}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial S}\right)_{Y,\{N_j\}}, \tag{2.89}$$

$$\left(\frac{\partial X}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial Y}\right)_{S,\{N_j\}}, \tag{2.90}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{S,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}}, \tag{2.91}$$

which relate seemingly diverse partial derivatives.

For a substance with a single type of molecule, Eqs. (2.84)–(2.91) become particularly simple if we work with densities. Let $h = H/n$ denote the molar enthalpy. Then the fundamental equation for the molar enthalpy can be written $h = u - xY = sT + \mu$. The exact differential of the molar enthalpy is $dh = Tds - xdY$ (for reversible processes), which yields the identities $(\partial h/\partial s)_Y = T$ and $(\partial h/\partial Y)_s = x$. Maxwell's relations reduce to $(\partial T/\partial Y)_s = -(\partial x/\partial s)_Y$. In Exercise 2.4, we compute the enthalpy for a monatomic ideal gas in terms of its natural variables.

■ **EXERCISE 2.4.** Compute the enthalpy for n moles of a monatomic ideal gas and express it in terms of its natural variables. The mechanical equation of state is $PV = nRT$ and the entropy is $S = \frac{5}{2}nR + nR\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$.

Answer: Let us write the molar entropy in terms of temperature and pressure. It is $s = \frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}]$. Also note that when $P = P_0$ and $T = T_0$, $s = s_0 = \frac{5}{2}R$. Now since $dh = Tds + vdP$ we have

$$\left(\frac{\partial h}{\partial s}\right)_P = T = T_0\left(\frac{P}{P_0}\right)^{2/5} e^{(s-s_0)/s_0} \tag{1}$$

and

$$\left(\frac{\partial h}{\partial P}\right)_s = +\frac{RT}{P}. \tag{2}$$

If we integrate, we find $h = \frac{5}{2}RT_0(P/P_0)^{2/5}e^{(s-s_0)/s_0} = \frac{5}{2}RT$. In terms of temperature, the enthalpy is $h = \frac{5}{2}RT$. There is an easier way to obtain these results. From Exercise 2.3, the molar internal energy is $u = \frac{3}{2}RT$. The fundamental equation for the molar enthalpy is $h = u + vP$, where $v = V/n$ is the molar volume. Since $v = RT/P$, we obtain $h = \frac{5}{2}RT$ and $H = \frac{5}{2}nRT$.

For a *YXT* system, the enthalpy is a thermodynamic potential for reversible processes carried out at constant Y. The discussion for the enthalpy is completely analogous to that for the internal energy except that now we allow the extensive variable X to change and maintain the system at constant Y. We then find

$$\Delta H \leq \int T\,dS - \int X\,dY - \Delta W_{\text{free}} + \sum_j \int \mu_j' dN_j, \tag{2.92}$$

where the equality holds for a reversible process and the inequality holds for a spontaneous process (ΔW_{free} is defined in Section 2.F.1). Therefore,

$$(\Delta H)_{S,Y,\{N_j\}} \leq (-\Delta W_{\text{free}}) \tag{2.93}$$

and we conclude that, *for a reversible process at constant S, Y, and $\{N_j\}$, work can be stored as enthalpy and can be recovered completely.*

If a process takes place at constant S, Y, and $\{N_j\}$ in which no work is done on or by the system, then

$$(\Delta H)_{S,Y,\{N_j\}} \leq 0. \tag{2.94}$$

Since the equilibrium state cannot change spontaneously, we find that *the equilibrium state at fixed S, Y, and $\{N_j\}$ is a state of minimum enthalpy.*

2.F.3. Helmholtz Free Energy

For processes carried out at constant T, X, and $\{N_j\}$, the Helmholtz free energy corresponds to a thermodynamic potential. The Helmholtz free energy, A, is useful for systems which are closed and thermally coupled to the outside world but are mechanically isolated (held at constant X). We obtain the Helmholtz free energy from the internal energy by adding a term due to the thermal coupling:

$$A = U - ST = YX + \sum_j \mu_j' N_j. \tag{2.95}$$

The addition of $-ST$ is a Legendre transformation which changes the independent variables from $(S, X, \{N_j\})$ to $(T, X, \{N_j\})$. If we take the differential of Eq. (2.95) and use Eq. (2.67), we find

$$dA \leq -S\,dT + Y\,dX + \sum_j \mu_j' dN_j. \tag{2.96}$$

Therefore,

$$S = -\left(\frac{\partial A}{\partial T}\right)_{X,\{N_j\}}, \tag{2.97}$$

$$Y = \left(\frac{\partial A}{\partial X}\right)_{T,\{N_j\}}, \tag{2.98}$$

and

$$\mu_j' = \left(\frac{\partial A}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}}. \tag{2.99}$$

Again, from Eq. (2.4), we obtain Maxwell relations

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}}, \tag{2.100}$$

$$\left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial T}\right)_{X,\{N_j\}}, \tag{2.101}$$

$$\left(\frac{\partial Y}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j'}{\partial X}\right)_{T,\{N_j\}}, \tag{2.102}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,X,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} \tag{2.103}$$

for the system.

We can write the corresponding equations in terms of densities. Let us consider a monatomic substance and let $a = A/n$ denote the molar Helmholtz free energy. Then the fundamental equations for the molar Helmholtz free energy is $a = u - sT = xY + \mu$. The combined first and second laws (for reversible processes) can be written $da = -s\,dT + Y\,dx$ so that $(\partial a/\partial T)_x = -s$

and $(\partial a/\partial x)_T = Y$. Maxwells relations reduce to $(\partial s/\partial x)_T = -(\partial Y/\partial T)_x$. In Exercise 2.5, we compute that Helmholtz free energy for a monatomic ideal gas in terms of its natural variables.

■ **EXERCISE 2.5.** Compute the Helmholtz free energy for n moles of a monatomic ideal gas and express it in terms of its natural variables. The mechanical equation of state is $PV = nRT$ and the entropy is $S = \frac{5}{2}nR + nR\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$.

Answer: Since $da = -sdT - Pdv$ we have

$$\left(\frac{\partial a}{\partial T}\right)_v = -s = -\frac{5}{2}R - R\ln\left[\frac{v}{v_0}\left(\frac{T}{T_0}\right)^{3/2}\right] \tag{1}$$

and

$$\left(\frac{\partial a}{\partial v}\right)_T = -P = -\frac{RT}{v}. \tag{2}$$

If we integrate, we find $a = -RT - RT\ln[(v/v_0)(T/T_0)^{3/2}]$ and $A = -nRT - nRT\ln[(V/V_0)(n_0/n)(T/T_0)^{3/2}]$.

For a *YXT* system, the Helmholtz free energy is a thermodynamic potential for reversible processes carried out at constant T, X, and $\{N_j\}$. For a change in the thermodynamic state of the system, the change in the Helmholtz free energy can be written

$$\Delta A \leq -\int S\,dT + \int Y\,dX - \Delta W_{\text{free}} + \sum_j \int \mu_j' dN_j, \tag{2.104}$$

where the inequality holds for spontaneous processes and the equality holds for reversible processes (ΔW_{free} is defined in Section 2.66). For a process carried out at fixed T, X, and $\{N_j\}$, we find

$$(\Delta A)_{T,X\{N_j\}} \leq (-\Delta W_{\text{free}}), \tag{2.105}$$

and we conclude that *for a reversible process at constant T, X, and $\{N_j\}$, work can be stored as Helmholtz free energy and can be recovered completely.*

If no work is done for a process occurring at fixed T, X, and $\{N_j\}$, Eq. (2.105) becomes

$$(\Delta A)_{T,X,\{N_j\}} \leq 0. \tag{2.106}$$

Thus, *an equilibrium state at fixed T, X, and $\{N_j\}$ is a state of minimum Helmholtz free energy.*

2.F.4. Gibbs Free Energy

For processes carried out at constant Y, T, and $\{N_j\}$, the Gibbs free energy corresponds to the thermodynamic potential. Such a process is coupled both thermally and mechanically to the outside world. We obtain the Gibbs free energy, G, from the internal energy by adding terms due to the thermal and mechanical coupling,

$$G = U - TS - XY = \sum_j \mu_j' N_j. \tag{2.107}$$

In this way we change from independent variables $(S, X, \{N_i\})$ to variables $(T, Y, \{N_i\})$. If we use the differential of Eq. (2.106) in Eq. (2.67), we obtain

$$dG \leq -S\,dT - X\,dY + \sum_j \mu_j' dN_j, \tag{2.108}$$

so that

$$S = -\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_j\}}, \tag{2.109}$$

$$X = -\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_j\}}, \tag{2.110}$$

and

$$\mu_j' = \left(\frac{\partial G}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}. \tag{2.111}$$

The Maxwell relations obtained from the Gibbs free energy are

$$\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}, \tag{2.112}$$

$$\left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial T}\right)_{Y,\{N_j\}}, \tag{2.113}$$

$$\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j'}{\partial Y}\right)_{T,\{N_j\}}, \tag{2.114}$$

and

$$\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i'}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} \tag{2.115}$$

and again relate seemingly diverse partial derivatives.

As we found in earlier sections, we can write the corresponding equations in terms of densities. We will consider a monomolecular substance and let $g = G/n$ denote the molar Gibbs free energy. Then the fundamental equation for the molar Gibbs free energy is $g = u - sT - xY = \mu$ and the molar Gibbs free energy is equal to the chemical potential (for a monomolelcular substance). The combined first and second laws (for reversible processes) can be written $dg = -sdT - xdY$ so that $(\partial g/\partial T)_Y = -s$ and $(\partial g/\partial Y)_T = -x$. Maxwells relations reduce to $(\partial s/\partial Y)_T = +(\partial x/\partial T)_Y$. For a monatomic substance, the molar Gibbs free energy is equal to the chemical potential.

For a *YXT* system, the Gibbs free energy is a thermodynamic potential for reversible processes carried out at constant T, Y, and $\{N_j\}$. For a change in the thermodynamic state of the system, the change in Gibbs free energy can be written

$$\Delta G \leq -\int S\,dT - \int X\,dY - \Delta W_{\text{free}} + \sum_j \int \mu_j'\,dN_j, \tag{2.116}$$

where the equality holds for reversible processes and the inequality holds for spontaneous processes (ΔW_{free} is defined in Section 2.F.1). For processes at fixed T, Y, and $\{N_j\}$, we obtain

$$(\Delta G)_{T,Y,\{N_j\}} \leq (-\Delta W_{\text{free}}). \tag{2.117}$$

Thus, *for a reversible process at constant T, Y, and $\{N_j\}$, work can be stored as Gibbs free energy and can be recovered completely.*

For a process at fixed T, Y, and $\{N_j\}$ for which no work is done, we obtain

$$(\Delta G)_{T,Y,\{N_j\}} \leq 0, \tag{2.118}$$

and we conclude that *an equilibrium state at fixed T, Y, and $\{N_j\}$ is a state of minimum Gibbs free energy.*

■ **EXERCISE 2.6.** Consider a system which has the capacity to do work, $đW = -Y\,dX + đW'$. Assume that processes take place spontaneously so that $dS = (1/T)đQ + d_iS$, where d_iS is a differential element of entropy due to the spontaneity of the process. Given the fundamental equation for the Gibbs free energy, $G = U - XY - TS$, show that $-(dG)_{Y,T} = đW' + Td_iS$. Therefore, at fixed Y and T, all the Gibbs free energy is available to do work for reversible processes. However, for spontaneous processes, the amount of work that can be done is diminished because part of the Gibbs free energy is used to produce entropy. This result is the starting point of nonequilibrium thermodynamics.

Answer: From the fundamental equation for the Gibbs free energy, we know that $dG = dU - X\,dY - Y\,dX - T\,dS - S\,dT$. Also we know that $dU = đQ + Y\,dX - đW'$, so we can write $dG = đQ - đW' - X\,dY - T\,dS - S\,dT$. For fixed Y and T we have $(dG)_{Y,T} = đQ - đW' - T\,dS$. Now remember that $dS = (1/T)đQ + d_iS$. Then we find $(dG)_{Y,T} = -đW' - Td_iS$. Note that the fundamental equation, $G = U - XY - TS$ contains the starting point of nonequilibrium thermodynamics.

For mixtures held at constant temperature, T, and pressure, P, the Gibbs free energy is a first-order homogeneous function of the particle numbers or particle mole numbers and this allows us to introduce a "partial" free energy, a "partial" volume, a "partial" enthalpy, and a "partial" entropy for each type of particle. For example, the chemical potential of a particle of type i, when written as $\mu_i = (\partial G/\partial n_i)_{T,P,\{n_{j\neq i}\}}$, is a partial molar Gibbs free energy. The total Gibbs free energy can be written

$$G = \sum_{i=1}^{N} n_i\mu_i = \sum_{i=1}^{n} n_i\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}. \tag{2.119}$$

The partial molar volume for a particle of type i is $v_i = (\partial V/\partial n_i)_{T,P,\{n_{j\neq i}\}}$, and the total volume can be written

$$V = \sum_{i=1}^{N} n_iv_i = \sum_{i=1}^{N} n_i\left(\frac{\partial V}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}. \tag{2.120}$$

The partial molar entropy for particle of type i is $s_i = (\partial S/\partial n_i)_{T,P,\{n_{j\neq i}\}}$, and the total entropy can be written

$$S = \sum_{i=1}^{N} n_is_i = \sum_{i=1}^{N} n_i\left(\frac{\partial S}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}. \tag{2.121}$$

Because the enthalpy is defined, $H = G + TS$, we can also define a partial molar enthalpy, $h_i = (\partial H/\partial n_i)_{T,P,\{n_{j\neq i}\}} = \mu_i + Ts_i$. Then the total enthalpy can be written $H = \sum_{i=1}^{N} n_ih_i$. These quantities are very useful when we describe the properties of mixtures in later chapters.

■ **EXERCISE 2.7.** Consider a fluid with electric potential, ϕ, containing ν different kinds of particles. Changes in the internal energy can be written, $dU = đQ - P\,dV + \phi de + \sum_j^{\nu} \mu_j dn_j$. Find the amount of Gibbs free energy needed to bring dn_i moles of charged particles of type i into the system at fixed temperature, pressure, and particle number, $n_j (j \neq i)$, in a reversible

manner. Assume that particles of type i have a valence, z_i. Note that the amount of charge in one mole of protons is called a *Faraday, F.*

Answer: The fundamental equation for the Gibbs free energy, $G = U + PV - TS$, yields $dG = dU + P\,dV + V\,dP - T\,dS - S\,dT$. Therefore, $dG = \not{d}Q + \phi de + \sum_j^\nu \mu_j dn_j + V\,dP - TdS - S\,dT$. For a reversible process, $dS = (1/T)\not{d}Q$, and $dG = \phi de + \sum_j^\nu \mu_j dn_j + V\,dP - S\,dT$. Now note that the charge carried by dn_i moles of particles of type, i, is $de = z_i F dn_i$. Thus, the change in the Gibbs free energy can be written

$$\begin{aligned} dG &= \phi de + VdP - SdT + \sum_j^\nu \mu_j dn_j \\ &= +V\,dP - S\,dT + (z_i F\phi + \mu_i)dn_i + \sum_{j\neq i}^\nu \mu_j dn_j. \end{aligned} \tag{1}$$

For fixed P, T, and $n_j (j \neq i)$, the change in the Gibbs free energy is

$$(dG)_{P,T,n_{j\neq i}} = (z_i F\phi + \mu_i)dn_i. \tag{2}$$

From Exercise 2.6, we see that this is just the work needed to add dn_i moles of charged particles of type, i, keeping all other quantities fixed. The quantity

$$\tilde{\mu}_i \equiv z_i F\phi + \mu_i, \tag{3}$$

is called the *electrochemical potential.*

2.F.5. Grand Potential

A thermodynamic potential which is extremely useful for the study of quantum systems is the grand potential. It is a thermodynamic potential energy for processes carried out in open systems where particle number can vary but T, X, and $\{\mu_j'\}$ are kept fixed.

The grand potential, Ω, can be obtained from the internal energy by adding terms due to thermal and chemical coupling of the system to the outside world:

$$\Omega = U - TS - \sum_j \mu_j' N_j = XY. \tag{2.122}$$

The Legendre transformation in Eq. (2.122) changes the independent variables from $(S, X, \{N_i\})$ to $(T, X, \{\mu_j'\})$. If we add the differential of Eq. (2.122) to Eq. (2.67), we obtain

$$d\Omega \leq -S\,dT + Y\,dX - \sum_j N_j d\mu_j', \tag{2.123}$$

and thus

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{X,\{\mu_j'\}}, \tag{2.124}$$

$$Y = \left(\frac{\partial \Omega}{\partial X}\right)_{T,\{\mu_j'\}}, \tag{2.125}$$

and

$$N_j = -\left(\frac{\partial \Omega}{\partial \mu_j'}\right)_{T,X,\{\mu_{l\neq j}'\}}. \tag{2.126}$$

The Maxwell relations obtained from the grand potential are

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{\mu_j'\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{\mu_j'\}}, \tag{2.127}$$

$$\left(\frac{\partial S}{\partial \mu_j'}\right)_{T,X,\{\mu_{l\neq j}'\}} = \left(\frac{\partial N_j}{\partial T}\right)_{X,\{\mu_i'\}}, \tag{2.128}$$

$$\left(\frac{\partial Y}{\partial \mu_j'}\right)_{T,X,\{\mu_{l\neq j}'\}} = -\left(\frac{\partial N_j}{\partial X}\right)_{T,\{\mu_i'\}}, \tag{2.129}$$

and

$$\left(\frac{\partial N_i}{\partial \mu_j'}\right)_{T,V,\{\mu_{l\neq j}'\}} = \left(\frac{\partial N_j}{\partial \mu_i'}\right)_{T,V,\{\mu_{l\neq i}'\}} \tag{2.130}$$

and are very useful in treating open systems. The grand potential is a thermodynamic potential energy for a reversible process carried out at constant T, X, and $\{\mu_j'\}$. For a change in the thermodynamic state of the system, the change in the grand potential can be written

$$\Delta\Omega \leq -\int S\,dT + \int Y\,dX - \Delta W_{\text{free}} - \sum_j \int N_j\,d\mu_j', \tag{2.131}$$

where the equality holds for reversible changes and the inequality holds for spontaneous changes (ΔW_{free} is defined in Section 2.F.1). For a process at fixed

T, X, and $\{\mu_j'\}$, we obtain

$$(\Delta\Omega)_{T,X,\{\mu_j'\}} \leq (-\Delta W_{\text{free}}). \tag{2.132}$$

Thus, *for a reversible process at constant T, X, and $\{\mu_j'\}$, work can be stored as grand potential and can be recovered completely.*

For a process at fixed T, X, and $\{\mu_j'\}$ for which no work is done, we obtain

$$(\Delta\Omega)_{T,X,\{\mu_j'\}} \leq 0, \tag{2.133}$$

and we find that *an equilibrium state at fixed T, X, and $\{\mu_j'\}$ is a state of minimum grand potential.*

2.G. RESPONSE FUNCTIONS

The response functions are the thermodynamic quantities most accessible to experiment. They give us information about how a specific state variable changes as other independent state variables are changed under controlled conditions. As we shall see in later chapters, they also provide a measure of the size of fluctuations in a thermodynamic system. The response functions can be divided into (a) thermal response functions, such as heat capacities, (b) mechanical response functions, such as compressibility and susceptibility, and (c) chemical response functions. We shall introduce some thermal and mechanical response functions in this section.

2.G.1. Thermal Response Functions (Heat Capacity)

The heat capacity, C, is a measure of the amount of heat needed to raise the temperature of a system by a given amount. In general, it is defined as the derivative, $C = (đQ/dT)$. When we measure the heat capacity, we try to fix all independent variables except the temperature. Thus, there are as many different heat capacities as there are combinations of independent variables, and they each contain different information about the system. We shall derive the heat capacity at constant X and $\{N_j\}$, $C_{X,\{N_j\}}$, and we shall derive the heat capacity at constant Y and $\{N_j\}$, $C_{Y,\{N_j\}}$. We will derive these heat capacities in two different ways, first from the first law and then from the definition of the entropy.

To obtain an expression of $C_{X,\{N_j\}}$, we shall assume that X, T, and $\{N_j\}$ are independent variables. Then the first law can be written

$$đQ = dU - Y\,dX - \sum_j \mu_j' dN_j = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} dT + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] dX$$
$$+ \sum_j \left[\left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} - \mu_j'\right] dN_j. \tag{2.134}$$

For constant X and $\{N_j\}$, we have $[đQ]_{X,\{N_j\}} = C_{X,\{N_j\}}dT$ and we find

$$C_{X,\{N_j\}} = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} \tag{2.135}$$

for the heat capacity at constant X and $\{N_j\}$.

To obtain an expression for $C_{Y,\{N_j\}}$, we shall assume that Y, T, and $\{N_j\}$ are independent variables. Then we can write

$$dX = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} dT + \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} dY + \sum_j \left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} dN_j. \tag{2.136}$$

If we substitute the expression for dX into Eq. (2.134), we obtain

$$\begin{aligned} đQ = &\left\{ C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \right\} dT \\ &+ \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} dY \\ &+ \sum_j \left\{ \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} + \left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} - \mu_j' \right\} dN_j. \end{aligned} \tag{2.137}$$

For constant Y and $\{N_j\}$ we have $[đQ]_{Y,\{N_j\}} = C_{Y,\{N_j\}}dT$ and we find

$$C_{Y,\{N_j\}} = C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \tag{2.138}$$

for the heat capacity at constant Y and $\{N_j\}$.

For n moles of a monatomic substance, these equations simplify. Let us write them in terms of molar quantities. We can write the heat capacity in the form $C_{X,n} = (\partial U/\partial T)_{X,n} = n(\partial u/\partial T)_x$, where $u = U/n$ is the molar internal energy and $x = X/n$ is a molar density of the mechanical extensive variable. The molar heat capacity is then $c_x = (\partial u/\partial T)_x$ so that $C_{X,n} = nc_x$. Similarly, let us note that $(\partial X/\partial T)_{Y,n} = n(\partial x/\partial T)_Y$ and $(\partial U/\partial X)_{T,n} = (\partial u/\partial x)_T$. Therefore, the molar heat capacity at constant Y is $c_Y = c_x + [(\partial u/\partial x)_T - Y]\ (\partial x/\partial T)_Y$.

It is useful to rederive expressions for $C_{X,\{N_j\}}$ and $C_{Y,\{N_j\}}$ from the entropy. Let us first assume that T, X, and $\{N_j\}$ are independent. Then for a reversible process, we obtain

$$đQ = T\,dS = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} dT + T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} dX + \sum_j T\left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} dN_j. \tag{2.139}$$

For a processes which occurs at constant X and $\{N_j\}$, Eq. (2.139) becomes

$$[đQ]_{X,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} dT, \tag{2.140}$$

and therefore

$$C_{X,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{X,\{N_j\}}. \tag{2.141}$$

The second term comes from Eq. (2.97).

Let us now assume that T, Y and $\{N_j\}$ are independent. For a reversible process, we obtain

$$đQ = T\,dS = T\left(\frac{\partial S}{\partial T}\right)_{Y,\{N_j\}} dT + T\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} dY + \sum_j T\left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} dN_j. \tag{2.142}$$

If we combine Eqs. (2.136) and (2.139), we can also write

$$\begin{aligned} đQ = T\,dS = T&\left[\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} + \left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}\right] dT \\ &+ T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} dY \\ &+ T\sum_j\left[\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} + \left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}}\right] dN_j. \end{aligned} \tag{2.143}$$

If we now compare Eqs. (2.142) and (2.143), we find

$$\begin{aligned} C_{Y,\{N_j\}} &= T\left(\frac{\partial S}{\partial T}\right)_{Y,\{N_j\}} = C_{X,\{N_j\}} + T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \\ &= -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{Y,\{N_j\}}. \end{aligned} \tag{2.144}$$

The last term in Eq. (2.144) comes from Eq. (2.109).

We can obtain some additional useful identities from the above equations. If we compare Eqs. (2.100), (2.138), and (2.144), we obtain the identity

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = \frac{1}{T}\left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}}. \tag{2.145}$$

Therefore,

$$\left(\frac{\partial^2 Y}{\partial T^2}\right)_{X,\{N_j\}} = -\frac{1}{T}\left(\frac{\partial C_{X,\{N_j\}}}{\partial X}\right)_{T,\{N_j\}}, \tag{2.146}$$

where we have used Eqs. (2.4) and (2.145).

For a monatomic substance, it is fairly easy to show that the molar heat capacity at constant mechanical molar density, x, is $c_x = T(\partial s/\partial T)_x = -T(\partial^2 a/\partial T^2)_x$, and the molar heat capacity at constant Y is $c_Y = T(\partial s/\partial T)_Y = -T(\partial^2 a/\partial T^2)_Y$. We also obtain the useful identities $(\partial s/\partial x)_T = (1/T)[(\partial u/\partial x)_T - Y] = -(\partial Y/\partial T)_x$ and $(\partial^2 Y/\partial T^{2])}_x = -(1/T)(\partial c_x/\partial x)_T$.

2.G.2. Mechanical Response Functions

There are three mechanical response functions which are commonly used. They are the *isothermal susceptibility*,

$$\chi_{T,\{N_j\}} = \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} = -\left(\frac{\partial^2 G}{\partial Y^2}\right)_{T,\{N_j\}}, \tag{2.147}$$

the *adiabatic susceptibility*,

$$\chi_{S,\{N_j\}} = \left(\frac{\partial X}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial^2 H}{\partial Y^2}\right)_{S,\{N_j\}}, \tag{2.148}$$

and the *thermal expansivity*,

$$\alpha_{Y,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}. \tag{2.149}$$

Using the identities in Section 2.B, the thermal and mechanical response functions can be shown to satisfy the identities

$$\chi_{T,\{N_j\}}(C_{Y,\{N_j\}} - C_{X,\{N_j\}}) = T(\alpha_{Y,\{N_j\}})^2, \tag{2.150}$$

$$C_{Y,\{N_j\}}(\chi_{T,\{N_j\}} - \chi_{S,\{N_j\}}) = T(\alpha_{Y,\{N_j\}})^2, \tag{2.151}$$

and

$$\frac{C_{Y,\{N_j\}}}{C_{X,\{N_j\}}} = \frac{\chi_{T,\{N_j\}}}{\chi_{S,\{N_j\}}}. \tag{2.152}$$

The derivation of these identities is left as a homework problem.

For *PVT* systems, the mechanical response functions have special names. Quantities closely related to the isothermal and adiabatic susceptibilities are the *isothermal compressibility,*

$$\kappa_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_j\}}, \tag{2.153}$$

and *adiabatic compressibility,*

$$\kappa_{S,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,\{N_j\}}, \tag{2.154}$$

respectively. The *thermal expansivity* for a *PVT* is defined slightly differently from above. It is

$$\alpha_{P,\{N_j\}} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\{N_j\}}. \tag{2.155}$$

For a monatomic *PVT* system the mechanical response functions become even simpler if written in terms of densities. The isothermal and adiabatic compressibilities are $\kappa_T = -(1/v)(\partial v/\partial P)_T$ and $\kappa_s = -(1/v)(\partial v/\partial P)_s$, respectively, where $u = V/n$ is the molar volume. The thermal expansivity is $\alpha_P = (1/v)(\partial v/\partial T)_P$.

■ **EXERCISE 2.8.** Compute the molar heat capacities, c_v and c_P, the compressibilities, κ_T and κ_s, and the thermal expansivity, α_P, for a monatomic ideal gas. Start from the fact that the molar entropy of the gas is $s = \frac{5}{2}R + R\ln[(v/v_0)(T/T_0)^{3/2}]$ ($v = V/N$ is the molar volume), and the mechanical equation of state is $Pv = RT$.

Answer:

(a) *The molar heat capacity,* c_v: The molar entropy is $s = \frac{5}{2}R + R\ln[(v/v_0)(T/T_0)^{3/2}]$. Therefore $(\partial s/\partial T)_v = (3R/2T)$ and $c_v = T(\partial s/\partial T)_v = 3R/2$.

(b) *The molar heat capacity,* c_P: The molar entropy can be written $s = \frac{5}{2}R + R\ln[(P_0/P)(T/T_0)^{5/2}]$. Then $(\partial s/\partial T)_P = 5R/2T$ and $c_P = T(\partial s/\partial T)_P = 5R/2$.

(c) *The isothermal compressibility,* κ_T: From the mechanical equation of state, we have $v = (RT/P)$. Therefore, $(\partial v/\partial P)_T = -(v/P)$ and $\kappa_T = -(1/v)(\partial v/\partial P)_T = (1/P)$.

(**d**) *The adiabatic compressibility*, κ_s: We must first write the molar volume as a function of s and P. From the expressions for the molar entropy and mechanical equation of state given above we find $v = v_0(P_0/P)^{3/5} \exp[(2s/5R) - 1]$. Then $(\partial v/\partial P)_s = -(3v/5P)$ and $\kappa_s = -(1/v)(\partial v/\partial P)_s = (3/5P)$.

(**e**) *Thermal Expansivity*, α_P: Using the mechanical equation of state, we find $\alpha_P = (1/v)(\partial v/\partial T)_P = (1/T)$.

2.H. STABILITY OF THE EQUILIBRIUM STATE

The entropy of an isolated equilibrium system (cf. Section 2.D.3) must be a maximum. However, for a system with a finite number of particles in thermodynamic equilibrium, the thermodynamic quantities describe the average behaviour of the system. If there are a finite number of particles, then there can be spontaneous fluctuations away from this average behaviour. However, fluctuations must cause the entropy to decrease. If this were not so, the system could spontaneously move to new equilibrium state with a higher entropy because of spontaneous fluctuations. For a system in a stable equilibrium state, this, by definition, cannot happen.

We can use the fact that the entropy must be maximum to obtain conditions for local equilibrium and for local stability of equilibrium systems. We will restrict ourselves to PVT systems. However, our arguments also apply to general YXT systems.

2.H.1. Conditions for Local Equilibrium in a PVT System

Let us consider a mixture of l types of particles in an isolated box of volume, V_T, divided into two parts, A and B, by a conducting porous wall which is free to move and through which particles can pass (cf. Fig. 2.8). With this type of dividing wall there is a free exchange of heat, mechanical energy, and particles between A and B. One can think of A and B as two different parts of a fluid (gas or liquid), or perhaps as a solid (part A) in contact with its vapor (part B). We shall assume that no chemical reactions occur. Since the box is closed and isolated, the total internal energy, U_T, is

$$U_T = \sum_{\alpha=A,B} U_\alpha, \tag{2.156}$$

where U_α is the internal energy of compartment α. The total volume, V_T, is

$$V_T = \sum_{\alpha=A,B} V_\alpha, \tag{2.157}$$

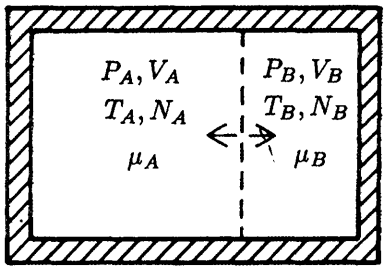


Fig. 2.8. An isolated, closed box containing fluid separated into two parts by a movable porous membrane.

where V_α is the volume of compartment α. The total number of particles, $N_{j,T}$, of type j is

$$N_{j,T} = \sum_{\alpha=A,B} N_{j,\alpha}, \tag{2.158}$$

where $N_{j,\alpha}$ is the total number of particles of type j in compartment α. The total entropy, S_T, is

$$S_T = \sum_{\alpha=A,B} S_\alpha, \tag{2.159}$$

where S_α is the total entropy of compartment α.

Let us now assume that spontaneous fluctuations can occur in the energy, volume, and particle number of each cell subject to the constraints

$$\Delta U_T = \Delta V_T = \Delta N_{j,T} = 0 \tag{2.160}$$

(assume that no chemical reactions occur) so that $\Delta U_A = -\Delta U_B$, $\Delta V_A = -\Delta V_B$, and $\Delta N_{j,A} = -\Delta N_{j,B}$. The entropy change due to these spontaneous fluctuations can be written

$$\Delta S_T = \sum_{\alpha=A,B} \left[\left(\frac{\partial S_\alpha}{\partial U_\alpha} \right)_{V_\alpha,\{N_{j,\alpha}\}} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right)_{U_\alpha,\{N_{j,\alpha}\}} \Delta V_\alpha + \sum_{j=1}^{l} \left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}} \right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}} \Delta N_{j,\alpha} \right] + \cdots \tag{2.161}$$

From Eqs. (2.58)–(2.60) and (2.160), we can write Eq. (2.161) in the form

$$\Delta S_T = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right) \Delta V_A - \sum_{j=1}^{l} \left(\frac{\mu'_{j,A}}{T_A} - \frac{\mu'_{j,B}}{T_B} \right) \Delta N_{j,A} + \cdots, \tag{2.162}$$

where T_α and P_α are the temperature and pressure, respectively, of the material in compartment α, and $\mu'_{j,\alpha}$ is the chemical potential of particles of type j in compartment α.

For a system in equilibrium, the entropy is a maximum. Therefore, any spontaneous changes must cause the entropy to decrease. However, $\Delta U_A, \Delta V_A$, and $\Delta N_{j,A}$ can be positive or negative. Thus, in order to ensure that $\Delta S_T \leq 0$, we must have

$$T_A = T_B, \tag{2.163}$$

$$P_A = P_B, \tag{2.164}$$

and

$$\mu'_{j,A} = \mu'_{j,B}, \qquad j = 1, \ldots, l. \tag{2.165}$$

Equations (2.163)–(2.165) give the conditions for local equilibrium in a system in which no chemical reactions occur. Thus, if the interface between A and B can transmit heat, mechanical energy, and particles of all types, then the two systems must have the same temperature, pressure, and chemical potential for each type of particle in order to be in equilibrium. It is important to note that if the partition cannot pass particles of type, i, then $\Delta N_{i,A} = \Delta N_{i,B} = 0$ and we can have $\mu'_{i,A} \neq \mu'_{i,B}$. If the partition is nonporous and fixed in position so no particles can pass and no mechanical work can be transmitted, then we can have $P_A \neq P_B$ and $\mu'_{j,A} \neq \mu'_{j,B}$ $(j = 1, \ldots, l)$ and still have equilibrium.

2.H.2. Conditions for Local Stability in a PVT System [12, 13]

Stability of the equilibrium state places certain conditions on the sign of the response functions. To see this, let us consider a closed isolated box with volume V_T, total entropy S_T, total internal energy U_T, and a total number of particles $N_{j,T}$ of type j, where $j = 1, \ldots, l$. We shall assume that the box is divided into M cells which can exchange thermal energy, mechanical energy, and particles. We shall denote the equilibrium volume, entropy, internal energy, and number of particles of type j for the αth cell by V^0_α, S^0_α, U^0_α, and $N^0_{j,\alpha}$, respectively. The equilibrium pressure, temperature, and chemical potentials of the various cells are P^0, T^0, and μ'^0_j, respectively (they must be the same for all the cells).

Because there are a finite number of particles in the box, there will be spontaneous fluctuations of the thermodynamic variables of each cell about their respective equilibrium values. These spontaneous fluctuations must be such that V_T, and U_T, and $N_{j,T}$ remain fixed. However, since the equilibrium state is stable, fluctuations must cause S_T to decrease. If it did not decrease, the equilibrium state would be unstable and spontaneous fluctuations would cause the system to move to a more stable equilibrium state of higher entropy.

We shall assume that fluctuations about the equilibrium state are small and expand the entropy of the αth cell in a Taylor expansion about its equilibrium value

$$
\begin{aligned}
&S_\alpha(U_\alpha, V_\alpha, \{N_{j,\alpha}\}) \\
&\quad = S^0_\alpha(U^0_\alpha, V^0_\alpha, \{N^0_{j,\alpha}\}) + \left(\frac{\partial S}{\partial U}\right)^0_{V,\{N_j\}} \Delta U_\alpha + \left(\frac{\partial S}{\partial V}\right)^0_{U,\{N_j\}} \Delta V_\alpha \\
&\qquad + \sum_{j=1}^{l} \left(\frac{\partial S}{\partial N_j}\right)^0_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha} + \frac{1}{2}\left\{ \Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}} \Delta U_\alpha \right. \\
&\qquad \left. + \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha,\{N_{j,\alpha}\}} \Delta V_\alpha + \sum_{j=1}^{l} \Delta\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}} \Delta N_{j,\alpha} \right\} + \cdots .
\end{aligned}
\tag{2.166}
$$

In Eq. (2.166), we define

$$
\begin{aligned}
\Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}} \equiv &\left(\frac{\partial^2 S}{\partial U^2}\right)^0_{V,\{N_j\}} \Delta U_\alpha + \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial U}\right)_{V,\{N_j\}}\right)^0_{U,\{N_j\}} \Delta V_\alpha \\
&+ \sum_{j=1}^{l} \left(\frac{\partial}{\partial N_j}\left(\frac{\partial S}{\partial U}\right)_{V,\{N_j\}}\right)^0_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha}.
\end{aligned}
\tag{2.167}
$$

A similar expression holds for $\Delta(\partial S_\alpha/\partial V_\alpha)_{U_\alpha,\{N_{j,\alpha}\}}$. For $\Delta(\partial S_\alpha/\partial N_{j,\alpha})_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}}$, we have

$$
\begin{aligned}
\Delta\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}} \equiv &\left(\frac{\partial}{\partial U}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,\{N_{k\neq j}\}}\right)^0_{V,\{N_j\}} \Delta U_\alpha \\
&+ \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,\{N_{k\neq j}\}}\right)^0_{U,\{N_j\}} \Delta V_\alpha \\
&+ \sum_{i=1}^{l} \left(\frac{\partial}{\partial N_i}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,\{N_{k\neq j}\}}\right)^0_{U,V,\{N_{k\neq i}\}} \Delta N_{i,\alpha}.
\end{aligned}
\tag{2.168}
$$

In Eqs. (2.166)–(2.168), the superscripts 0 on partial derivatives indicate that they are evaluated at equilibrium. The fluctuations $\Delta U_\alpha, \Delta V_\alpha$, and $\Delta N_{j,\alpha}$ are defined as $\Delta U_\alpha = U_\alpha - U^0_\alpha, \Delta V_\alpha = V_\alpha - V^0_\alpha$, and $\Delta N_{j,\alpha} = N_{j,\alpha} - N^0_{j,\alpha}$ and denote the deviation of the quantities U_α, V_α, and $N_{j,\alpha}$ from their absolute equilibrium values.

We can obtain the total entropy by adding the contributions to the entropy from each of the M cells. Because the entropy can only decrease due to fluctuations, the terms which are first order in the fluctuations, ΔU_α, ΔV_α, and $\Delta N_{j,\alpha}$ must add to zero (this is just the condition for local equilibrium obtained in Section 2.H.1). Therefore, the change in the entropy due to fluctuations must have the form

$$\Delta S_T = \frac{1}{2}\sum_{\alpha=1}^{M}\left\{\Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}}\Delta U_\alpha + \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha,\{N_{j,\alpha}\}}\Delta V_\alpha + \sum_{j=1}^{l}\Delta\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}}\Delta N_{j,\alpha}\right\} + \cdots. \tag{2.169}$$

Equation (2.169) can be written in simpler form if we make use of Eqs. (2.58)–(2.60). We than find

$$\Delta S_T = \frac{1}{2}\sum_{\alpha=1}^{M}\left[\Delta\left(\frac{1}{T}\right)_\alpha \Delta U_\alpha + \Delta\left(\frac{P}{T}\right)_\alpha \Delta V_\alpha - \sum_{j=1}^{l}\Delta\left(\frac{\mu_j'}{T}\right)_\alpha \Delta N_{j,\alpha}\right] + \cdots \tag{2.170}$$

or

$$\Delta S_T = -\frac{1}{2T}\sum_{\alpha=1}^{M}\left[\Delta T_\alpha \Delta S_\alpha - \Delta P_\alpha \Delta V_\alpha + \sum_{j=1}^{l}\Delta\mu_{j,\alpha}'\Delta N_{j,\alpha}\right] + \cdots. \tag{2.171}$$

In Eq. (2.171), we have used the relation $T\Delta S = \Delta U + P\Delta V - \sum_{j=1}^{l}\mu_j'\Delta N_j$. Equation (2.171) gives the entropy change, due to spontaneous fluctuations, in a completely general form. We can now expand ΔS_T in terms of any set of independent variables we choose.

Let us choose T, P, and N_j as the independent variables. Then we can write

$$\Delta S_\alpha = \left(\frac{\partial S}{\partial T}\right)^0_{P,\{N_j\}}\Delta T_\alpha + \left(\frac{\partial S}{\partial P}\right)^0_{T,\{N_j\}}\Delta P_\alpha + \sum_{j=1}^{l}\left(\frac{\partial S}{\partial N_j}\right)^0_{T,P,\{N_{k\neq j}\}}\Delta N_{j,\alpha}, \tag{2.172}$$

$$\Delta V_\alpha = \left(\frac{\partial V}{\partial T}\right)^0_{P,\{N_j\}}\Delta T_\alpha + \left(\frac{\partial V}{\partial P}\right)^0_{T,\{N_j\}}\Delta P_\alpha + \sum_{j=1}^{l}\left(\frac{\partial V}{\partial N_j}\right)^0_{T,P,\{N_{k\neq j}\}}\Delta N_{j,\alpha}, \tag{2.173}$$

and

$$\Delta\mu'_{j,\alpha} = \left(\frac{\partial\mu'_j}{\partial T}\right)^0_{P,\{N_j\}} \Delta T_\alpha + \left(\frac{\partial\mu'_j}{\partial P}\right)^0_{T,\{N_j\}} \Delta P_\alpha + \sum_{i=1}^{l} \left(\frac{\partial\mu'_j}{\partial N_i}\right)^0_{T,P,\{N_{k\neq i}\}} \Delta N_{i,\alpha}. \tag{2.174}$$

If we now substitute Eqs. (2.172)–(2.174) into Eq. (2.171) and use the Maxwell relations (2.112)–(2.115), the entropy change becomes

$$\Delta S_T = -\frac{1}{2T}\sum_{\alpha=1}^{M}\left[\left(\frac{\partial S}{\partial T}\right)^0_{P,\{N_j\}} (\Delta T_\alpha)^2 - 2\left(\frac{\partial V}{\partial T}\right)^0_{P,\{N_j\}} \Delta T_\alpha \Delta P_\alpha - \left(\frac{\partial V}{\partial P}\right)^0_{T,\{N_j\}} (\Delta P_\alpha)^2 + \sum_{i=1}^{l}\sum_{j=1}^{l}\left(\frac{\partial\mu'_j}{\partial N_i}\right)^0_{T,P,\{N_{k\neq i}\}} \Delta N_{i,\alpha}\Delta N_{j,\alpha}\right] + \cdots. \tag{2.175}$$

If we make use of Eqs. (2.6), (2.8) and (2.100), we can write

$$\left(\frac{\partial S}{\partial T}\right)_{P,\{N_j\}} = \left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} - \left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}} \left(\frac{\partial V}{\partial T}\right)^2_{P,\{N_j\}}. \tag{2.176}$$

If we plug this into Eq. (2.175), we obtain

$$\Delta S_T = -\frac{1}{2T}\sum_{\alpha=1}^{M}\left[\left(\frac{\partial S}{\partial T}\right)^0_{V,\{N_j\}} (\Delta T_\alpha)^2 - \left(\frac{\partial P}{\partial V}\right)^0_{T,\{N_j\}} [\Delta V_\alpha]^2_{\{N_j\}} + \sum_{i=1}^{l}\sum_{j=1}^{l}\left(\frac{\partial\mu'_j}{\partial N_i}\right)^0_{T,P,\{N_{k\neq i}\}} \Delta N_{i,\alpha}\Delta N_{j,\alpha}\right] + \cdots, \tag{2.177}$$

where

$$[\Delta V_\alpha]_{\{N_j\}} \equiv \left(\frac{\partial V}{\partial T}\right)^0_{P,\{N_j\}} \Delta T_\alpha + \left(\frac{\partial V}{\partial P}\right)^0_{T,\{N_j\}} \Delta P_\alpha. \tag{2.178}$$

Because the fluctuations ΔT_α, ΔP_α, and $\Delta N_{j,\alpha}$ are independent, the requirement that $\Delta S_T \leq 0$ for a stable equilibrium state leads to the requirement that

$$C_{V,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} \geq 0, \qquad \kappa_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} \geq 0,$$

$$\text{and} \qquad \sum_{i=1}^{l}\sum_{j=1}^{l}\left(\frac{\partial\mu'_j}{\partial N_i}\right)_{T,P,\{N_{k\neq i}\}} \Delta N_i \Delta N_j \geq 0. \tag{2.179}$$

Conditions (2.179) are a realization of Le Châteliers's famous principle: *If a system is in stable equilibrium, then any spontaneous change in its parameters must bring about processes which tend to restore the system to equilibrium.*

The first condition in Eq. (2.179), $C_{V,\{N_j\}} \geq 0$, is a condition for *thermal stability.* If a small excess of heat is added to a volume element of fluid, then the temperature of the volume element must increase relative to its surroundings so that some of the heat will flow out again. This requires that the heat capacity be positive. If the heat capacity were negative, the temperature would decrease and even more heat would flow in, thus leading to an instability. From Eqs. (2.150) and (2.179) we can also show that

$$C_{P,\{N_j\}} > C_{V,\{N_j\}} \geq 0. \tag{2.180}$$

The second condition in Eq. (2.179), $\kappa_{T,\{N_j\}} \geq 0$, is a condition for *mechanical stability.* If a small volume element of fluid spontaneously increases, the pressure of the fluid inside the fluid element must decrease relative to its surroundings so that the larger pressure of the surroundings will stop the growth of the volume element. This requires that the compressibility be positive. If the compressibility were negative, the pressure would increase and the volume element would continue to grow, thus leading to an instability. From Eqs. (2.151) and (2.179) we can show that

$$\kappa_{T,\{N_j\}} > \kappa_{S,\{N_j\}} \geq 0. \tag{2.181}$$

The third condition, $\sum_{i=1}^{l}\sum_{j=1}^{l}(\partial\mu'_j/\partial N_i)_{T,P,\{N_{k\neq i}\}}\,\Delta N_i \Delta N_j \geq 0$, where ΔN_i and ΔN_j are arbitrary variations, is the condition for *chemical stability.* We can write the condition for chemical stability in matrix form:

$$(\Delta N_1, \Delta N_2, \ldots, \Delta N_l)\begin{pmatrix} \mu'_{1,1} & \mu'_{1,2} & \cdots & \mu'_{1,l} \\ \mu'_{2,1} & \mu'_{2,2} & \cdots & \mu'_{2,l} \\ \vdots & \vdots & \ddots & \vdots \\ \mu'_{l,1} & \mu'_{l,2} & \cdots & \mu'_{l,l} \end{pmatrix}\begin{pmatrix} \Delta N_1 \\ \Delta N_2 \\ \vdots \\ \Delta N_l \end{pmatrix} \geq 0, \tag{2.182}$$

where $\mu'_{j,i} \equiv (\partial\mu'_j/\partial N_i)_{T,P,\{N_{k\neq i}\}}$. Because of the Maxwell relation $\mu'_{j,i} = \mu'_{i,j}$ [cf. Eq. (2.115)], the matrix

$$\bar{\mu}' \equiv \begin{pmatrix} \mu'_{1,1} & \mu'_{1,2} & \cdots & \mu'_{1,l} \\ \mu'_{2,1} & \mu'_{2,2} & \cdots & \mu'_{2,l} \\ \vdots & \vdots & \ddots & \vdots \\ \mu'_{l,1} & \mu'_{l,2} & \cdots & \mu'_{l,l} \end{pmatrix} \tag{2.183}$$

is symmetric. In addition, in order to satisfy the condition for chemical stability, the matrix $\bar{\mu}'$ must be a positive definite matrix. A symmetric matrix is

positive definite if $\mu_{ii} > 0$ $(i = 1, \ldots, l)$ and if every principal minor is positive or zero.

■ **EXERCISE 2.9.** A mixture of particles, A and B, has a Gibbs free energy of the form

$$G = n_A\mu_A^0(P,T) + n_B\mu_B^0(P,T) + RTn_A\ln(x_A) + RTn_B\ln(x_B) + \lambda\frac{n_An_B}{n},$$

where $n = n_A + n_B, x_A = n_A/n$, and $x_B = n_B/n$ (n indicates mole number), μ_A^0 and μ_B^0 are functions only of P and T. Plot the region of thermodynamic instability in the $x_A - T$ plane.

Answer: For chemical stability, the matrix

$$\begin{pmatrix} \mu_{A,A} & \mu_{A,B} \\ \mu_{B,A} & \mu_{B,B} \end{pmatrix}$$

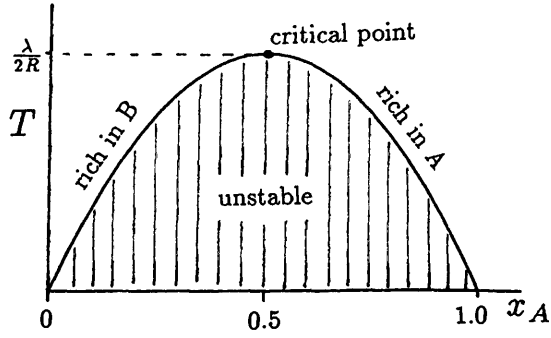
must be symmetric positive definite. This requires that $(\partial\mu_A/\partial n_A)_{P,T,n_B} > 0$, $(\partial\mu_B/\partial n_B)_{P,T,n_A} > 0$, and $(\partial\mu_A/\partial n_B)_{P,T,n_A} = (\partial\mu_B/\partial n_A)_{P,T,n_B} < 0$. The chemical potential of the A-type particle is

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} = \mu_A^0(P,T) + RT\ln(x_A) + \lambda\frac{n_B}{n} - \lambda\frac{n_An_B}{n^2}. \qquad (2)$$

A condition for thermodynamic stability is

$$\left(\frac{\partial\mu_A}{\partial n_A}\right)_{P,T,n_B} = \frac{RT}{x_A}\frac{n_B}{n^2} - 2\frac{\lambda n_B}{n^2} + 2\frac{\lambda n_An_B}{n^3} > 0, \qquad (3)$$

or $x_A^2 - x_A + RT/2\lambda > 0$. For $T > \lambda/2R$, this is always satisfied. A plot of $T = (2\lambda/R)(x_A - x_A^2)$ is given below.



The shaded region corresponds to $x_A^2 - x_A + RT/2\lambda < 0$ and is thermodynamically unstable. The unshaded region is thermodynamically stable. For $T < \lambda/2R$, two values of x_A satisfy the condition $x_A^2 - x_A + RT/2\lambda > 0$ for

each value of T. These two values of x_A lie outside and on either side of the shaded region and are the mole fractions of two coexisting phases of the binary mixture, one rich in A and the other rich in B. For $T > \lambda/2R$, only one value of x_A satisfies the condition $x_A^2 - x_A + RT/2\lambda > 0$, so only one phase of the substance exists. (As we shall see in Chapter 3, a thermodynamically stable state may not be a state of thermodynamic equilibrium. For thermodynamic equilibrium we have the additional condition that the free energy be minimum or the entropy be maximum. A thermodynamically stable state which is not an equilibrium state is sometimes called a *metastable* state. It can exist in nature but eventually will decay to an absolute equilibrium state.)

2.H.3. Implications of the Stability Requirements for the Free Energies

The stability conditions place restrictions on the derivatives of the thermodynamic potentials. Before we show this, it is useful to introduce the concept of concave and convex functions [14]:

(**a**) A function $f(x)$ is a *convex* function if $d^2f(x)/dx^2 \geq 0$ for all x (cf. Fig. 2.9). For any x_1 and x_2 the chord joining the points $f(x_1)$ and $f(x_2)$ lies above or on the curve $f(x)$ for all x in the interval $x_1 < x < x_2$. If $df(x)/dx$ exists at a given point, the tangent at that point always lies below the function except at the point of tangency.

(**b**) A function $f(x)$ is a *concave* function of x if the function $-f(x)$ is convex.

We can now consider the effect of the stability requirements on the Helmholtz and Gibbs free energies.

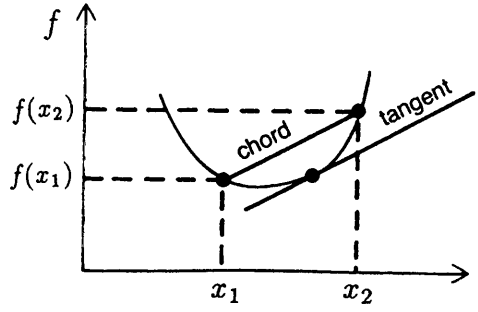


Fig. 2.9. The function $f(x)$ is a convex function of x.

From Eq. (2.97) and the stability condition, Eq. (2.180), we can write

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} = -\frac{C_{V,\{N_j\}}}{T} < 0, \tag{2.184}$$

and from Eq. (2.98) and the stability condition, Eq. (2.181), we can write

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,\{N_j\}} = -\left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}} = \frac{1}{V\kappa_{T,\{N_j\}}} > 0 \tag{2.185}$$

The Helmholtz free energy is a concave function of temperature and a convex function of volume.

From Eq. (2.109) and the stability condition, Eq. (2.180), we can write

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{P,\{N_j\}} = -\frac{C_{P,\{N_j\}}}{T} < 0, \tag{2.186}$$

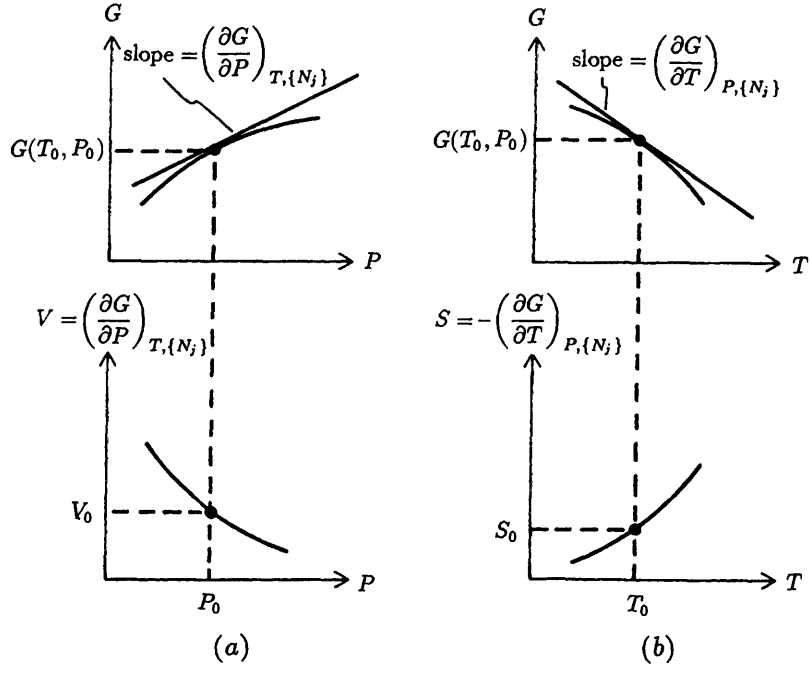


Fig. 2.10. (a) A plot of the Gibbs free energy and its slope as a function of pressure. (b) A plot of the Gibbs free energy and its slope as a function of temperature. Both plots are done in a region which does not include a phase transition.

and from Eq. (2.110) and the stability condition, Eq. (2.181), we can write

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_j\}} = \left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} = -V\kappa_{T,\{N_j\}} < 0, \tag{2.187}$$

Thus, *the Gibbs free energy is a concave function of temperature and a concave function of pressure.*

It is interesting to sketch the free energy and its slope as function of pressure and temperature. A sketch of the Gibbs free energy, for a range of pressure and temperature for which no phase transition occurs, is given in Fig. 2.10. The case of phase transitions is given in Chapter 3.

The form of the Gibbs and Helmholtz free energies for a magnetic system is not so easy to obtain. However, Griffiths [15] has shown that for system of uncharged particles with spin, $G(T,H)$ is a concave function of T and H and $A(T,M)$ is a concave function of T and convex function of M. In Fig. 2.11, we sketch the Gibbs free energy and its slope as a function of T and H for a paramagnetic system.

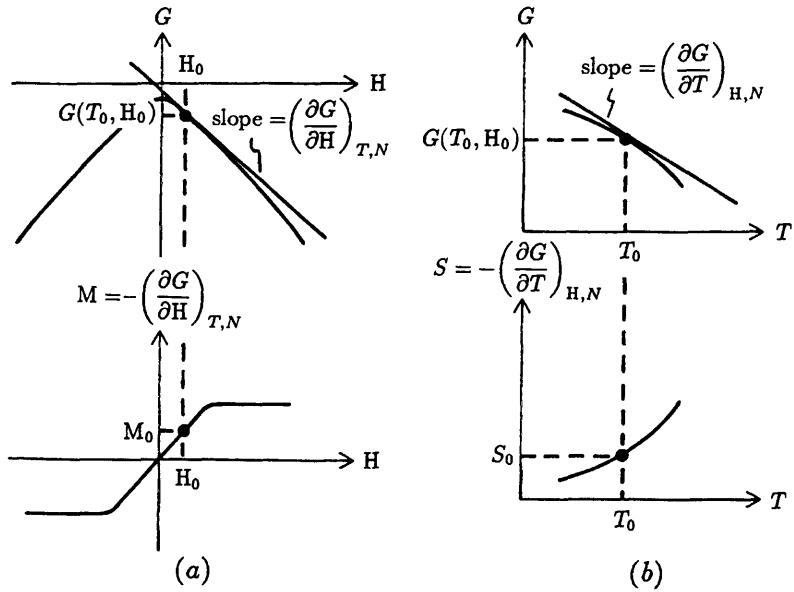


Fig. 2.11. (a) A plot of the Gibbs free energy and its slope as a function of applied field. (b) A plot of the Gibbs free energy and its slope as a function of temperature. Both plots are done in a region which does not include a phase transition.

▶ SPECIAL TOPICS

▶ S2.A. Cooling and Liquefaction of Gases [6]

All neutral gases (if we exclude gravitational effects) interact via a potential which has a hard core and outside the core a short-ranged attractive region. If such a gas is allowed to expand, it must do work against the attractive forces and its temperature will decrease. This effect can be used to cool a gas, although the amount of cooling that occurs via this mechanism alone is very small. We shall study two different methods for cooling: one based solely on free expansion and one which involves throttling of the gas through a porous plug or constriction. The second method is the basis for gas liquefiers commonly used in the laboratory.

▶ S2.A.1. The Joule Effect: Free Expansion

Experiments which attempted to measure cooling due to free expansion were first performed by Gay-Lussac in 1807 and were improved upon by Joule in 1843. The free expansion process is shown schematically in Fig. 2.12. The gas is initially confined to an insulated chamber with volume V_i at pressure P_i and temperature T_i. It is then allowed to expand suddenly into an insulated evacuated chamber with volume V_f. Since the gas expands freely, no work will be done and $\Delta W = 0$. Furthermore, since both chambers are insulated, no heat will be added and $\Delta Q = 0$. Thus, from the first law the internal energy must remain constant, $\Delta U = 0$, during the process. The only effect of free expansion is a transfer of energy between the potential energy and kinetic energy of the particles.

Because free expansion takes place spontaneously, the entropy of the gas will increase even though no heat is added. During the expansion we cannot use thermodynamics to describe the state of the system because it will not be in equilibrium, even locally. However, after the system has settled down and

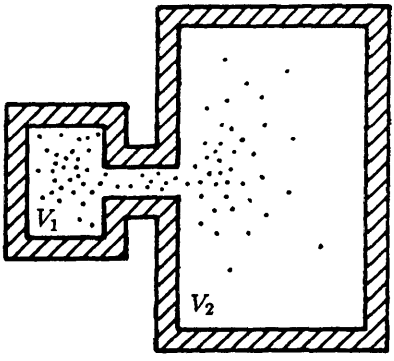


Fig. 2.12. The Joule effect. Free expansion of a gas from an insulated chamber of volume, V_1, into an insulated evacuated chamber of volume, V_2, causes cooling.

reached a final equilibrium state, we can use the thermodynamics to relate the initial and final states by finding an imaginary reversible path between them.

During the expansion the internal energy does not change and the particle number does not change. Thus, the internal energies and particle numbers of the initial and final states must be the same, and for our imaginary reversible path we can write

$$[dU]_n = 0 = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV, \tag{2.188}$$

where n is the number of moles of gas. From Eq. (2.188), we can write

$$dT = -\frac{\left(\frac{\partial U}{\partial V}\right)_{T,n}}{\left(\frac{\partial U}{\partial T}\right)_{V,n}} dV = \left(\frac{\partial T}{\partial V}\right)_{U,n} dV, \tag{2.189}$$

where we have made use of the chain rule, Eq. (2.6). The quantity $(\partial T/\partial V)_{U,n}$ is called the *Joule coefficient.*

Let us compute the Joule coefficient for various gases. From Eq. (2.145), we know that

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P. \tag{2.190}$$

For an ideal gas we have the equation of state, $PV = nRT$, and we find that $(\partial U/\partial V)_{T,n} = 0$. Therefore, for an ideal gas the Joule coefficient, $(\partial T/\partial V)_{U,n} = 0$, and the temperature of an ideal gas cannot change during free expansion.

For a van der Waals gas [cf. Eq. (2.12)], we have

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = \frac{an^2}{V^2}. \tag{2.191}$$

For this case, there will be a change in internal energy due to interactions as volume changes if temperature is held fixed. To obtain the Joule coefficient, we must also find the heat capacity of the van der Waals gas. From Eq. (2.146), we obtain

$$\left(\frac{\partial C_{V,n}}{\partial V}\right)_{T,n} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,n} = 0. \tag{2.192}$$

Therefore, for a van der Waals gas the heat capacity, $C_{V,n}$, is independent of volume and can depend only on mole number and temperature:

$$C_{V,n} = C_{V,n}(T, n). \tag{2.193}$$

Since the heat capacity, $C_{V,n}$, contains no volume corrections due to interactions, it is thermodynamically consistent to choose its value to be equal to that of an ideal gas (at least in the regime where the van der Waals equation describes a gas). If we neglect internal degrees of freedom, we can write $C_{V,n} = \frac{3}{2}nR$. The Joule coefficient for a van der Waals gas then becomes

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = -\frac{2}{3}\frac{an}{RV^2}. \tag{2.194}$$

Using Eq. (2.194), we can integrate Eq. (2.189) between initial and final states. We find

$$T_f = \frac{2an}{3R}\left(\frac{1}{V_f} - \frac{1}{V_i}\right) + T_i. \tag{2.195}$$

The fractional change in temperature is therefore

$$\bar{\Delta}T = \left(\frac{T_f - T_i}{T_i}\right) = \frac{2an}{3RT_i}\left(\frac{1}{V_f} - \frac{1}{V_i}\right). \tag{2.196}$$

If $V_f > V_i$, the temperature will always decrease. We can use values of the van der Waals constant, a, given in Table 2.1 to estimate the change in temperature for some simple cases. Let us assume that $V_i = 10^{-3}\,\mathrm{m}^3$, $T_i = 300\,\mathrm{K}$, $n = 1$ mol, and $V_f = \infty$ (this will give maximum cooling). For oxygen we have $\bar{\Delta}T \approx -0.037$, and for carbon dioxide we obtain, $\bar{\Delta}T \approx -0.097$. We must conclude that free expansion alone is not a very effective way to cool a gas.

▶ S2.A.2. The Joule–Kelvin Effect: Throttling

Throttling of a gas through a porous plug or a small constriction provides a much more efficient means of cooling than free expansion and is the basis of most liquification machines. The throttling process in its simplest form is depicted in Fig. 2.13. A gas initially at a pressure, P_i, temperature, T_i, and volume, V_i, is forced through a porous plug into another chamber, maintained at pressure, $P_f < P_i$. All chambers and the plug are insulated so $\Delta Q = 0$ for the process. The gas inside the plug is forced through narrow twisting chambers irreversibly. Work must be done to force the gas through the plug. Even though the entire process is irreversible, we can use thermodynamics to relate the initial and final states.

The net work done by the gas is

$$\Delta W = \int_0^{V_f} P_f dV + \int_{V_i}^{0} P_i dV = P_f V_f - P_i V_i. \tag{2.197}$$

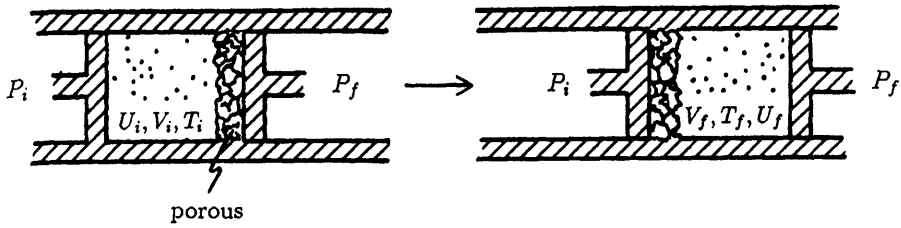


Fig. 2.13. The Joule–Kelvin effect. Throttling of a gas through a porous plug can cause cooling or heating.

From the first law, $\Delta U = -\Delta W$ since $\Delta Q \equiv 0$. Thus,

$$U_f + P_f V_f = U_i + P_i V_i \tag{2.198}$$

or, in terms of enthalpy,

$$H_f = H_i. \tag{2.199}$$

Thus, the throttling process is one which takes place at constant enthalpy.

Let us now construct a hypothetical reversible path to describe the constant enthalpy process. For each differential change along the reversible path, we have (assuming the total particle number remains constant)

$$[dH]_n = 0 = T\,dS + V\,dP. \tag{2.200}$$

We see that the increase in entropy due to the throttling process is accompanied by a decrease in pressure. It is convenient to use temperature and pressure as independent variables rather than entropy and pressure. We therefore expand the entropy

$$[dS]_n = \left(\frac{\partial S}{\partial T}\right)_{P,n} dT + \left(\frac{\partial S}{\partial P}\right)_{T,n} dP \tag{2.201}$$

and obtain

$$[dH]_n = 0 = C_{P,n} dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,n}\right] dP. \tag{2.202}$$

In Eq. (2.202) we have used Eqs. (2.144) and (2.112). Equation (2.202) can be rewritten in the form

$$dT = \left(\frac{\partial T}{\partial P}\right)_{H,n} dP, \tag{2.203}$$

where $(\partial T/\partial P)_{H,n}$ is the *Joule–Kelvin coefficient* and is defined

$$\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_{H,n} = -\frac{\left(\frac{\partial H}{\partial P}\right)_{T,n}}{\left(\frac{\partial H}{\partial T}\right)_{P,n}} = \frac{1}{C_{P,n}}\left[T\left(\frac{\partial V}{\partial T}\right)_{P,n} - V\right]. \tag{2.204}$$

Let us now compute the Joule–Kelvin coefficient for various gases. For an ideal gas, $(\partial V/\partial T)_{P,n} = (V/T)$ and therefore the Joule–Kelvin coefficient, $(\partial T/\partial P)_{H,n}$, equals 0. There will be no temperature change during the throttling process for an ideal gas. Furthermore, since $T_i = T_f$ for ideal gases, $P_f V_f = P_i V_i$ and no net work will be done ($\Delta W = 0$). If work had been done on or by the gas, we would expect a temperature change since the process is adiabatic.

For a van der Waals gas, assuming that $C_{V,n} = \frac{3}{2}nR$, we find

$$\left(\frac{\partial T}{\partial P}\right)_{H,n} = \frac{1}{R}\left[\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 - b\right] \Bigg/ \left[\frac{5}{2} - \frac{3a}{RTv}\left(\frac{v-b}{v}\right)^2\right], \tag{2.205}$$

where $v = V/n$ is the molar volume. Equation (2.205) is straightforward to obtain from the righthand term in Eg. (2.204) and from Egs. (2.12), (2.144), and (2.100). For an interacting gas, such as the van der Waals gas, the Joule–Kelvin coefficient can change sign. This is easiest to see if we consider low densities so that $RTv \gg a$ and $v \gg b$. Then

$$\left(\frac{\partial T}{\partial P}\right)_{H,n} \approx \frac{2}{5R}\left[\frac{2a}{RT} - b\right]. \tag{2.206}$$

For low temperatures $(\partial T/\partial P)_{H,n} > 0$, and gases cool in the throttling process, but at high temperatures, we have $(\partial T/\partial P)_{H,n} < 0$, and they heat up. Two effect determine the behaviour of the Joule–Kelvin coefficient. On the one hand, the gas expand, which gives rise to cooling. On the other hand, work can be done on or by the gas. If $P_i V_i > P_f V_f$, then net work is done on the gas, which causes heating. If $P_i V_i < P_f V_f$, then net work is done by the gas, which causes cooling.

The inversion temperature (the temperature at which the sign of μ_{JK} changes) for the Joule–Kelvin coefficient will be a function of pressure. Since $C_{P,n} > 0$, the condition for inversion [from Eq. (2.204)] is

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{V}{T} \tag{2.207}$$

or, for a van der Waals gas [cf. Eq. (2.205)],

$$\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 = b. \tag{2.208}$$

We can use the van der Waals equation, (2.12), to write Eq. (2.208) in terms of pressure and temperature. First solve Eq. (2.208) for v as a function R, T, a, and b, and substitute into the van der Waals equation. This gives

$$P = \frac{2}{b}\sqrt{\frac{2aRT}{b} - \frac{3RT}{2b} - \frac{a}{b^2}}. \tag{2.209}$$

The inversion curve predicted by the van der Waals equation has the shape of a parabola with a maximum at $T_{\max}^{VW} = 8a/9bR$. For CO_2, $T_{\max}^{VW} = 911\,\mathrm{K}$ while the experimental value [15] is $T_{\max}^{VW} = 1500\,\mathrm{K}$. For H_2, $T_{\max}^{VW} = 99\,\mathrm{K}$ while the experimental value [15] is $T_{\max}^{VW} = 202\,\mathrm{K}$. In Fig. 2.14, we plot the van der Waals and the experimental inversion curves for N_2. The van der Waals equation predicts an inversion curve which lies below the experimental curve but qualitatively has the correct shape. For nitrogen at $P = 10^5\,\mathrm{Pa}$, $\mu_{JK} = 1.37 \times 10^{-7}\,\mathrm{K/Pa}$ at $T = 573\,\mathrm{K}$, $\mu_{JK} = 1.27 \times 10^{-6}\,\mathrm{K/Pa}$ at $T = 373\,\mathrm{K}$, $\mu_{JK} = 6.40 \times 10^{-6}\,\mathrm{K/Pa}$ at $T = 173\,\mathrm{K}$, and $\mu_{JK} = 2.36 \times 10^{-5}\,\mathrm{K/Pa}$ at $T = 93\,\mathrm{K}$. (For experimental value of μ_{JK} for other substances, see the International Critical Tables [5].) We see that the cooling effect can be quite large for throttling.

A schematic drawing of a liquefaction machine which utilizes the Joule–Kelvin effect is shown in Fig. 2.15. Gas is precooled in a vessel, A, below its inversion temperature and expanded through a small orifice into vessel, B, thus causing it to cool due to the Joule–Kelvin effect. The cooled gas is allowed to circulate about the tube in B so that the gas in the tube becomes progressively

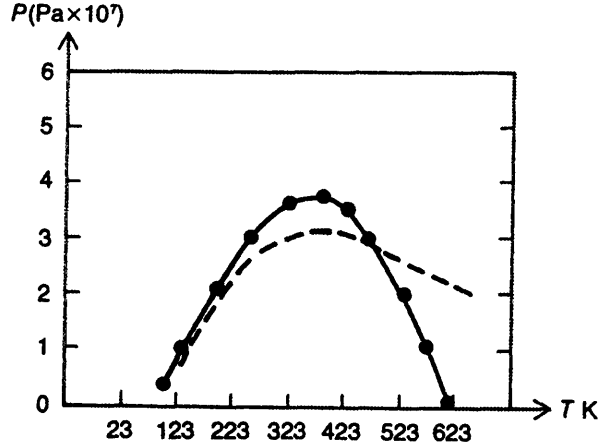


Fig. 2.14. A plot of the inversion temperature versus pressure for the Joule–Kelvin coefficient of N_2. The solid line is the experimental curve [6]. The dashed line is the curve predicted by the van der Waals equation for $a = 0.1408$ Pa. $\mathrm{M}^6/\mathrm{mol}^2$ and $b = 0.03913\mathrm{m}^3/\mathrm{mol}$.

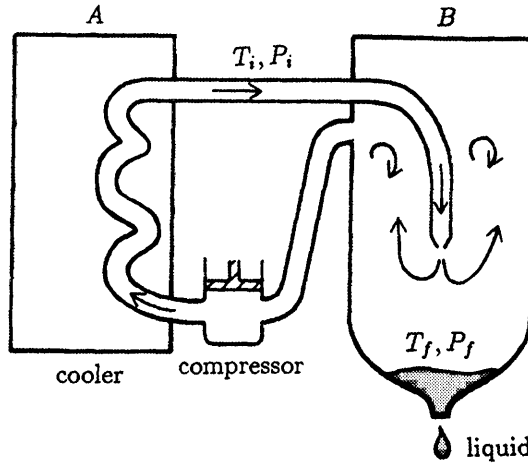


Fig. 2.15. Schematic drawing of a gas liquefier using the Joule–Kelvin effect.

cooler before expanding through the orifice. The process is run continuously and eventually the gas liquefies and collects below.

At times the Joule–Kelvin effect can lead to serious difficulties. For example, highly compressed H_2, which has a low inversion temperature, can ignite spontaneously when leaking from a damaged container, because of Joule–Kelvin heating.

▶ S2.B. Entropy of Mixing and the Gibbs Paradox [6]

If entropy is a measure of disorder in a system, then we expect that an entropy increase will be associated with the mixing of distinguishable substances, since this causes an increase in disorder. As we shall now show, this does indeed occur even for ideal gases.

Let us consider an ideal gas containing n_1 moles of atoms of type A_1, n_2 moles of atoms of type $A_2, \ldots$, and n_m moles of atoms of type A_m in a box of volume V and held at temperature T. The equation of state for the ideal gas mixture can be written

$$P = \sum_{j=1}^{m} P_j, \tag{2.210}$$

where P_j is the pressure of the j th component (partial pressure) and is defined as follows:

$$P_j = \frac{n_j RT}{V}. \tag{2.211}$$

The mole fraction of atoms of type A_j is defined as follows:

$$x_j = \frac{n_j}{\sum_{i=1}^{m} n_i} = \frac{P_j}{P}. \tag{2.212}$$

The change in the Gibbs free energy for an arbitrary change in the variables, $P, T, n_1, \ldots, n_m$, is

$$dG = -S\,dT + V\,dP + \sum_{j=1}^{m} \mu_j dn_j, \tag{2.213}$$

where μ_j is the chemical potential and S, V, and μ_j are given by Eqs. (2.109)–(2.111), but with mole number replacing particle number.

Let us now find the entropy of mixing for a mixture of distinguishable monatomic ideal gases. The Gibbs free energy of n moles of a monatomic ideal gas is

$$G(T, P, n) = -nRT \ln\left[\frac{T^{5/2}}{P}\right] + G^{(0)}, \tag{2.214}$$

where $G^{(0)}$ is a constant [cf. Eq. (2.107) and Exercise 2.3]. We will first consider a box held at temperature T and pressure P partitioned into m compartments, and let us assume the following: compartment 1 contains n_1 moles of atoms of type A_1 at pressure P and temperature T; compartment 2 contains n_2 moles of atoms of type A_2 at pressure P and temperature T; and so on. The compartments are separated by walls that can transmit heat and mechanical energy, so the pressure and temperature is uniform throughout the system. The Gibbs free energy of the system is the sum of the free energies of each compartment and can be written

$$G_I(P, T, n_1, \ldots, n_m) = -\sum_{j=1}^{m} n_j RT \ln\left[\frac{T^{5/2}}{P}\right] + G_I^{(0)}, \tag{2.215}$$

where $G_I^{(0)}$ is a constant. If we now remove the partitions and let the gases mix so that the final temperature and pressure are T and P, the Gibbs free energy of the mixture will be

$$\begin{aligned} G_F(P, T, n_1, \ldots, n_m) &= -\sum_{j=1}^{m} n_j RT \ln\left[\frac{T^{5/2}}{P_j}\right] + G_F^{(0)} \\ &= G_I(P, T, n_1, \ldots, n_m) + \sum_{j=1}^{m} n_j RT \ln(x_j) + G_F^{(0)} - G_I^{(0)}, \end{aligned} \tag{2.216}$$

where $G_F^{(0)}$ is a constant and we have used the relation $P_j = Px_j$. The change in the Gibbs free energy during the mixing process is therefore

$$\Delta G = G_F - G_I = \sum_{j=1}^{m} n_j RT \ln(x_j) + G_F^{(0)} - G_I^{(0)}. \tag{2.217}$$

From Eqs. (2.109) and (2.217), the increase in entropy due to mixing is

$$\Delta S_{\text{mix}} = -\sum_{j=1}^{m} n_j R \ln(x_j). \tag{2.218}$$

If $x_j = 1$ (one compartment and one substance), then $\Delta S_{\text{mix}} \equiv 0$, as it should be. If there are two compartments, each containing one mole, then $x_1 = (1/2)$ and $x_2 = (1/2)$ and $\Delta S_{\text{mix}} = 2R\ln(2)$ and the entropy increases during mixing.

It is important to note that Eq. (2.218) contains no explicit reference to the type of particles in the various compartments. As long as they are different, mixing increases the entropy. However, if they are identical, Eq. (2.218) tells us that there will still be an increase in entropy when the partitions are removed, even though the concept of mixing loses its meaning. Clearly, Eq. (2.218) does not work for identical particles. This was first noticed by Gibbs and is called the *Gibbs paradox*. The resolution of the Gibbs paradox lies in quantum mechanics, as we shall see when we come to statistical mechanics, (cf. Chapter 7). Identical particles must be counted in a different way from distinguishable particles (they have different "statistics"). This difference between identical and distinguishable particles persists even in the classical limit and leads to a resolution of the Gibbs paradox.

▶ S2.C. Osmotic Pressure in Dilute Solutions

Each spring, when the weather begins to warm up, sap rises in the trees, and the yearly cycle of life starts again. The rising of sap is one of many examples in biological systems of the phenomenon called *osmosis*. We can easily demonstrate the effect in the laboratory. Let us take a beaker of water and immerse a long tube (open at both ends) in it. The water levels of the tube and of the beaker will be the same. Next, close off the bottom end of the tube with a membrane which is permeable to water but not sugar. The water levels will still be the same in the tube and the beaker. Now add a bit of sugar to the water in the tube. Water will begin to enter the tube through the membrane, and the level of the sugar solution will rise a distance h above the level of the water in the beaker (cf. Fig. 2.16). The excess pressure created in the tube, $\pi = \rho_s hg$, is called the *osmotic pressure* (ρ_s is the density of the sugar solution and g is the acceleration of gravity). After equilibrium is reached, the pressure on the side of the membrane with sugar solution will be greater than that on the water side, by a factor π. The membrane must sustain the unbalanced force.

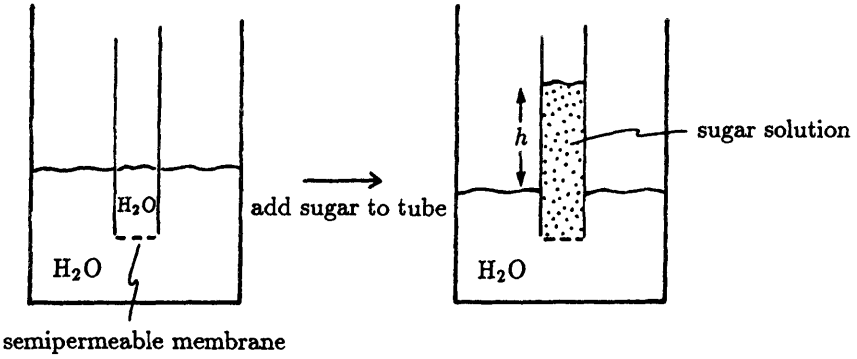


Fig. 2.16. The osmotic pressure of the sugar solution is $\pi = \rho_s hg$, where ρ_s is the density of the sugar solution and g is the acceleration of gravity.

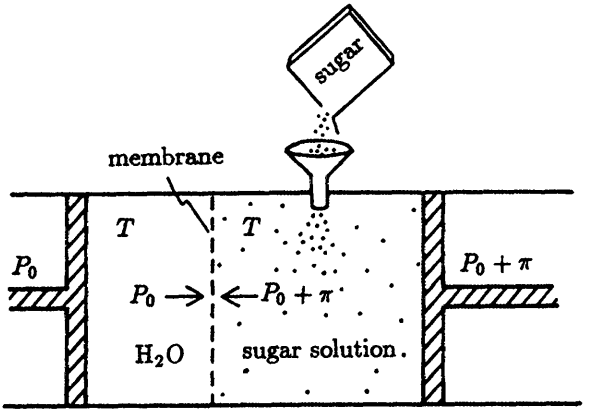


Fig. 2.17. A schematic representation of osmosis.

It is instructive to show the same phenomenon in another way (cf. Fig. 2.17). We will consider a system consisting of pure water, separated by a permeable (to water) membrane from a solution of sugar and water. The entire system is kept at a fixed temperature T, and the membrane is rigid. At equilibrium, there will be an imbalance in the pressures of the two sides. If P_0 is the pressure of the pure water, than the sugar solution will have a pressure $P = P_0 + \pi$, where π is the *osmotic pressure*. This imbalance of pressures is possible because the membrane is rigid and cannot transmit mechanical energy. Since the water is free to move through the membrane, the chemical potential of the pure water must be equal to the chemical potential of the water in the sugar solution.

Let us first write the thermodynamic relations for this system. First consider the sugar solution. A differential change in the Gibbs free energy, $G =$

$G(P, T, n_w, n_s)$, of the sugar solution (with n_w moles of water and n_s moles of sugar solution) can be written

$$dG = -S\,dT + V\,dP + \mu_w dn_w + \mu_s dn_s, \tag{2.219}$$

where $S = -(\partial G/\partial T)_{P,n_w,n_s}$ is the entropy of the solution, $V = (\partial G/\partial P)_{T,n_w,n_s}$ is the volume of the solution, and $\mu_w = (\partial G/\partial n_w)_{P,T,n_s}$ and $\mu_s = (\partial G/\partial n_s)_{P,T,n_w}$ are the chemical potentials of the water and sugar, respectively, in the solution. The chemical potentials are intensive and depend only on ratios n_s/n_w. It is convenient to introduce mole fractions

$$x_w = \frac{n_w}{n_w + n_s} = \frac{1}{1 + n_s/n_w} \quad \text{and} \quad x_s = \frac{n_s}{n_w + n_s} = \frac{n_s/n_w}{1 + n_s/n_w}. \tag{2.220}$$

Since $x_w + x_s = 1$, the chemical potentials can be written as a function of mole fraction, x_s. Thus, $\mu_w = \mu_w(P, T, x_s)$ and $\mu_s = \mu_s(P, T, x_s)$.

At equilibrium the chemical potentials of the pure water and the water in the sugar solution will be equal. If we let $\mu_w^{(0)}(P_0, T)$ denote the chemical potential of the pure water, we can write

$$\mu_w^{(0)}(P_0, T) = \mu_w(P, T, x_s) \tag{2.221}$$

as the condition for thermodynamic equilibrium.

We want to obtain an expression for the osmotic pressure in terms of measurable quantities. We will simplify properties of the solution as much as possible. We will assume that the solution is dilute so that $n_s/n_w \ll 1$ and $x_s \approx n_s/n_w \ll 1$. We can construct a fairly simple model to describe the solution. We write the Gibbs free energy of the solution in the form

$$\begin{aligned} G(P, T, n_s, n_w) = {} & n_w \mu_w^{(0)}(P, T) + n_s \mu_s^{(0)}(P, T) - \lambda \frac{n_s n_w}{n} \\ & + n_w RT \ln(x_w) + n_s RT \ln(x_s). \end{aligned} \tag{2.222}$$

The chemical potential $\mu_w^{(0)}(\mu_s^{(0)})$ contains contributions to the Gibbs free energy due to the presence of water (sugar) molecules and due to self-interactions. The term $-\lambda(n_s n_w/n)$ gives the contribution to the free energy due to interactions between sugar and water molecules. The last two terms on the right give contributions to the free energy due to mixing [cf. Eq. 3.57]. The chemical potential of the water in the solution can now be written

$$\mu_w(P, T, x_s) = \left(\frac{\partial G}{\partial n_w}\right)_{P,T,n_s} = \mu_w^{(0)}(P, T) - \lambda x_s^2 + RT \ln(1 - x_s), \tag{2.223}$$

where $\mu_w^{(0)}(P, T)$ is the chemical potential of pure water at pressure P and temperature T. For a dilute solution, $x_s = n_s/n \ll 1$ and $\ln(1 - x_s) =$

$-x_s - (1/2)x_s^2 - \cdots$. Thus, to lowest order in $x_s = n_s/n$, we find

$$\mu_w(P, T, x_s) \approx \mu_w^{(0)}(P, T) - x_s RT \tag{2.224}$$

for the chemical potential of water in a dilute sugar solution.

We now can find an expression for the osmotic pressure, $\pi = P - P_0$. Let us note that water, as well as most liquids, is very incompressible. The compressibility, κ_T, of water at 0 °C is $\kappa_T = 4.58 \times 10^{-11}$ cm^2/dyne. Therefore the quantity $(\partial\mu_w^0/\partial P)_{T,n_w} = (\partial V^0/\partial n_w)_{T,P} \equiv v_w^0$ (v_w^0 is the partial molar volume of water in the absence of solute and V^0 is the volume of water in the absence of solute) remains approximately constant for small changes in pressure. With this observation we can integrate $(\partial\mu_w^0/\partial P)_{T,n_w}$ to find

$$\mu_w^0(P, T) - \mu_w^0(P_0, T) \approx v_w^0(P - P_0) = v_w^0\pi. \tag{2.225}$$

Let us now assume that the change in the volume of water as we increase the number of moles is proportional to the number of moles so that $V^0 = n_w v_w^0$. Also, for very small concentrations of solute, we can assume that the change in the volume of water due to the presence of the solute is negligible so that $V^0 \approx V$, where V is the volume of the mixture. Then we can combine Eqs. (2.221), (2.224), and (2.225) to obtain

$$\pi \approx \frac{n_s RT}{V}. \tag{2.226}$$

Equation (2.226) is called *van't Hoff's law* and, surprisingly, looks very much like the ideal gas law, although we are by no means dealing with a mixture of ideal gases. Equation (2.226) is well verified for all dilute neutral solvent–solute systems.

■ **EXERCISE 2.10.** An experiment is performed in which the osmotic pressure of a solution, containing n_{suc} moles of sucrose ($C_{12}H_{22}O_{11}$) and 1 kg of water (H_2O), is found to have the following values [2]: (a) for $n_{suc} = 0.1, \pi = 2.53 \times 10^5$ Pa, (b) for $n_{suc} = 0.2, \pi = 5.17 \times 10^5$ Pa, and (c) for $n_{suc} = 0.3, \pi = 7.81 \times 10^5$ Pa. Compute the osmotic pressure of this system using van't Hoff's law. How do the computed values compare with the measured values?

Answer: The molecular weight of water (H_2O) is $M_{H_2O} = 18$ gr/mol. Therefore, 1 kg of water contains 55.56 mol of water. The molar volume of water is $v_{H_2O} = 18 \times 10^{-6}$ m^3/mol. The osmotic pressure of the solution, according to van't Hoff's law, is

$$\pi = \frac{n_{suc}}{55.56} \frac{(8.317\,\text{J/K})(303\,\text{K})}{18 \times 10^{-6}\,\text{m}^3/\text{mol}}.$$

The computed values are as follows: (a) For $n_{suc} = 0.1$, $\pi = 2.52 \times 10^5$ Pa, (b) for $n_{suc} = 0.2, \pi = 5.04 \times 10^5$ Pa, and (c) for $n_{suc} = 0.3, \pi = 7.56 \times 10^5$ Pa. The predictions of van't Hoff's law are good for a dilute solution of sucrose in water, but begin to deviate as the mole fraction of sucrose increases.

▶ S2.D. The Thermodynamics of Chemical Reactions [16–18]

Chemical reactions occur in systems containing several species of molecules (which we will call A, B, C, and D), which can transform into one another through inelastic collisions. A typical case might be one in which molecules A and B can collide inelastically to form molecules C and D. Conversely, molecules C and D can collide inelastically to form molecules A and B. The collisions occur at random and can be either elastic or inelastic. To be inelastic and result in a reaction, the two molecules must have sufficient energy to overcome any potential barriers to the reaction which might exist. Chemical equilibrium is a dynamical state of the system. It occurs when the rate of production of each chemical species is equal to its rate of depletion through chemical reactions. The chemical reactions themselves never stop, even at equilibrium.

In the early part of this century a Belgium scientist, de Donder, found that it was possible to characterize each chemical reaction by a single variable ξ, called the *degree of reaction*. In terms of ξ, it is then possible to determine when the Gibbs free energy has reached its minimum value (chemical reactions usually take place in systems with fixed temperature and pressure) and therefore when the chemical system reaches chemical equilibrium. It is important to notice that the concept of degree of reaction assumes that we can generalize the concept of Gibbs free energy to systems out of equilibrium.

▶ S2.D.1. The Affinity

Let us consider a chemical reaction of the form

$$-\nu_A A - \nu_B B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \nu_C C + \nu_D D. \tag{2.227}$$

The quantities ν_A, ν_B, ν_C, and ν_D are called *stoichiometric coefficients*; ν_j is the number of molecules of type j needed for the reaction to take place. By convention, ν_A and ν_B are negative. The constant k_1 is the rate constant for the forward reaction, and k_2 is the rate constant for the backward reaction. The rate constants give the probability per unit time that a chemical reaction takes place. If the rate constants are known, then one can find the rate of change in the

number of each type of molecule involved in the chemical reaction. For example, the rate of change in the number, N_A, of molecules of type A is given by

$$\frac{dN_A}{dt} = -k_1 N_A^{|\nu_A|} N_B^{|\nu_B|} + k_2 N_C^{|\nu_C|} N_D^{|\nu_D|}, \tag{2.228}$$

where $|\nu_A|$ denotes the absolute value of ν_A. Equation (2.228) reflects the fact that $|\nu_A|$ molecules of A and $|\nu_B|$ molecules of B must collide to destroy A molecules while $|\nu_C|$ molecules of C and $|\nu_D|$ molecules of D must collide to create A molecules.

Let us now assume that initially there are $n_A = -\nu_A n_0$ moles of A, $n_B = -\nu_B n_0 + N_B$ moles of B, $n_C = \nu_C n_0'$ moles of C, and $n_D = \nu_D n_0' + N_D$ moles of D. The reaction to the right will be complete when

$$n_A = 0, \qquad n_B = N_B, \qquad n_C = \nu_C(n_0 + n_0'), \qquad n_D = \nu_D(n_0 + n_0') + N_D.$$

We next define the *degree of reaction* by the equation

$$\xi = (n_0 + n_0') + \frac{n_A}{\nu_A}. \tag{2.229}$$

As we have defined it, ξ has the units of moles. In terms of ξ, the number of moles of each substance can be written

$$n_A = -\nu_A(n_0 + n_0') + \nu_A \xi, \tag{2.230}$$

$$n_B = -\nu_B(n_0 + n_0') + N_B + \nu_B \xi, \tag{2.231}$$

$$n_C = \nu_C \xi, \tag{2.232}$$

and

$$n_D = \nu_D \xi + N_D. \tag{2.233}$$

Any changes in the concentrations due to the reaction can therefore be written

$$dn_A = \nu_A d\xi, \quad dn_B = \nu_B d\xi, \quad dn_C = \nu_C d\xi, \quad dn_D = \nu_D d\xi \tag{2.234}$$

or

$$\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} = d\xi. \tag{2.235}$$

Equations (2.234) and (2.235) are very important because they tell us that any

changes in the thermodynamic properties of a system due to a given reaction can be characterized by a single variable.

From Eq. (2.108), differential changes in the Gibbs free energy may be written

$$dG = -S\,dT + V\,dP + \sum_{j=1}^{m} \mu_j dn_j = -S\,dT + V\,dP + \sum_{j=1}^{m} \mu_j \nu_j d\xi, \qquad (2.236)$$

where the sum is over the species which participate in the reaction. Therefore

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \sum_{j=1}^{m} \mu_j \nu_j, \qquad (2.237)$$

and the quantity

$$A \equiv \sum_{j=1}^{m} \mu_j \nu_j \qquad (2.238)$$

is called the *affinity* (in some books the affinity is defined with an opposite sign). At chemical equilibrium, the Gibbs free energy must be a minimum,

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T}^{0} = A^0 = 0 \qquad (2.239)$$

(the superscript 0 denotes equilibrium) and, therefore, at chemical equilibrium the affinity must be zero.

We can easily find the sign of the affinity as the system moves toward chemical equilibrium from the left or right. At constant P and T, the Gibbs free energy, G, must always decrease as the system moves toward chemical equilibrium (at equilibrium G is a minimum). Therefore,

$$[dG]_{P,T} = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} d\xi < 0. \qquad (2.240)$$

If the reaction goes to the right, then $d\xi > 0$ and $A < 0$. If the reaction goes to the left, then $d\xi < 0$ and $A > 0$. This decrease in the Gibbs free energy is due to spontaneous entropy production resulting from the chemical reactions (see Exercise 2.6).

If there are r chemical reactions in the system involving species, j, then there will be r parameters, ξ_k, needed to describe the rate of change of the number of moles, n_j:

$$dn_j = \sum_{k=1}^{r} \nu_{jk} d\xi_k. \qquad (2.241)$$

Table 2.2. Values of the Chemical Potential, μ^0, for Some Molecules in the Gas Phase at Pressure $P_0 = 1$ atm and Temperature $T_0 = 298$ K

Molecule	μ^0 (kcal/mol)
H_2	0.00
HI	0.31
I_2	4.63
N_2	0.00
NO_2	12.39
NH_3	−3.98
N_2O_4	23.49

The sum over k is over all chemical reactions in which molecules of type j participate.

Using ideal gas laws, some useful relations can be obtained for reactions in the gas phase. Consider a gas composed of four different kinds of molecules (A, B, C, and D) which undergo the reaction in Eq. (2.227). If the partial pressure of the ith constituent is P_i, the chemical potential of the ith constituent can be written

$$\mu_i(P_i, T) = \mu_i^0(P_0, T_0) - RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P_i}\right)\right], \tag{2.242}$$

where $\mu_i^0(P_0, T_0)$ is the chemical potential of the ith constituent at pressure P_0 and temperature T_0. Values of μ_i^0, with $P_0 = 1$ atm and $T_0 = 298$ K, have been tabulated for many kinds of molecules [20]. A selection is given in Table 2.2. If we use Eq. (2.242), the Gibbs free energy can be written

$$\begin{aligned} G(T, P, \xi) &= \sum_i n_i \mu_i = \sum_i n_i \mu_i^0(P_0, T_0) - \sum_i n_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P_i}\right)\right] \\ &= \sum_i n_i \mu_i^0(P_0, T_0) - \sum_i n_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] \\ &\quad + RT \ln[x_A^{n_A} x_B^{n_B} x_C^{n_C} x_D^{n_D}], \end{aligned} \tag{2.243}$$

and the affinity can be written

$$\begin{aligned} A(T,P,\xi) &= \sum_i \nu_i \mu_i^0(P_0,T_0) - \sum_i \nu_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P_i}\right)\right] \\ &= \sum_i \nu_i \mu_i^0(P_0,T_0) - \sum_i \nu_i RT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] \\ &\quad + RT \ln\left[\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}}\right], \end{aligned} \tag{2.244}$$

where $P = \sum_i P_i$ is the pressure and T is the temperature at which the reaction occurs.

For "ideal gas reactions" the equilibrium concentrations of the reactants can be deduced from the condition that at equilibrium the affinity is zero, $A^0 = 0$. From Eq. (2.243) this gives the equilibrium condition

$$\ln\left[\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}}\right] = \sum_i \nu_i \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right)\right] - \frac{1}{RT}\sum_i \nu_i \mu_i^0(P_0,T_0), \tag{2.245}$$

where $P_0 = 1$ atm and $T_0 = 298$ K. Equation (2.245) is called the *law of mass action*. As we shall show in Exercise 2.11, we can use it to compute the value of the degree of reaction, and therefore the mole fractions, at which chemical equilibrium occurs as a function of pressure and temperature.

▶ S2.D.2. Stability

Given the fact that the Gibbs free energy for fixed P and T is minimum at equilibrium, we can deduce a number of interesting general properties of chemical reactions. First, let us note that at equilibrium we have

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T}^0 = A^0 = 0 \tag{2.246}$$

and

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T}^0 = \left(\frac{\partial A}{\partial \xi}\right)_{P,T}^0 > 0. \tag{2.247}$$

Equations (2.246) and (2.247) are statements of the fact that the Gibbs free energy, considered as a function of P, T, and ξ, is minimum at equilibrium for fixed T and P.